DEVELOPMENT OF OPERATIONAL STRATEGIES TO MINIMIZE BROMATE FORMATION IN THE MOORHEAD WATER TREATMENT PLANT

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Title

Development of Operational Strategies to Minimize Bromate Formation in the Moorhead Water Treatment Plant

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

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ABSTRACT

A recent study at the Moorhead water treatment plant (MWTP) determined that bromate formed during ozone disinfection and, at times, exceeded the maximum contaminant level (MCL) of 10 parts per billion (ppb) in the summer months. Operational data showed that bromate formation was directly related to raw water bromide concentration and control of the ozone system. This study was conducted with the purpose of developing and implementing operational strategies to minimize bromate formation in the MWTP. Several operational changes, including selection of source water based on bromide concentration and controlling ozone addition in a manner that reduces the ozone dose used to achieve disinfection, were implemented and were effective at minimizing bromate formation in the ozone chambers. The bromate concentration in the finished drinking water was significantly reduced and only a few samples contained greater than 10 ppb bromate.

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Finally, thank you Mom, Dad, Kerri, and Brianna for your love and support. Thank you to the rest of my family, friends, and love ones who always put a smile on my face. Without your encouragement I wouldn’t have been able to complete this.

DEDICATION

To my godson Grady Robert.

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AOP	advanced oxidation process
APHA	American Public Health Association
ASCE	American Society of Civil Engineers
AWWA	American Water Works Association
CT	concentration x time
D/DBP	Disinfectants/Disinfection By-products
DOC	dissolved organic carbon
EDA	ethylenediamine
EOP	electrochemical oxidation potential
HRT	hydraulic retention time
MDH	Minnesota Department of Health
MDL	minimum detection limit
MCL	maximum contaminant level
MGD	million gallons per day
MPS	Moorhead Public Service
MRL	minimum reporting limit
MWTP	Moorhead Water Treatment Plant
NOM	natural organic matter
NTU	Nephelometric Turbidity Unit
ppb	parts per billion
ppm	parts per million
PSA	pressure swing adsorption
QA/QC	quality assurance/quality control
SCADA	Supervisory Control and Data Acquisition
SM	Standard Methods
SUVA	Specific Ultraviolet Absorbance

TOBr	Total Organobromine
TOC	total organic carbon
T&O	taste and odor
USEPA	United States Environmental Protection Agency
WEF	Water Environment Federation
μ	average
σ	standard deviation

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CHAPTER 1. INTRODUCTION

A recent study at the Moorhead Water Treatment Plant (MWTP) determined that bromate forms during ozonation and, at times, exceeds the maximum contaminant limit (MCL) of 10 parts per billion (ppb) (Storlie, 2013). These findings are significant because the bromate ion has been identified as a carcinogen that has caused kidney tumors in laboratory animals (Symons & Zheng, 1997) and increases the risk of cancer after long-term exposure at levels above the MCL (Jurenka, 2009).

Regulatory compliance for bromate is determined using a running annual average that is computed from monthly samples. If the average concentration of consecutive samples taken over a one-year period exceeds the MCL, the public water supply is out of compliance and must notify the public and report the violation to their reporting agency (Pontius & Diamond, 1999). The Stage 1 Disinfection/Disinfection By-Products (D/DBP) Rule requires the collection of one bromate sample from the entry point to the distribution system per month (USEPA, 2001).

The purposes of this study are to develop and implement operational changes to minimize bromate formation in the MWTP, and to gain a better understanding of factors that affect bromate formation during ozonation. Although the MWTP has never violated the Stage 1 D/DBP Rule, this study is essential for achieving better control of bromate formation to ensure future compliance. This study is important because most research in literature has been conducted on the laboratory- or pilot-scales, which do not always reflect full-scale conditions because water quality parameters and operational controls are more complicated in full-scale systems. Also, the vast majority of these studies have been conducted under conditions that do not simulate operating conditions at the MWTP. For example, most research has been conducted at near neutral pH, whereas the MWTP ozonation system is operated at a pH ranging from approximately 9.0 to 10.6. For these reasons, full-scale studies are required to better understand bromate formation and to assist ozone facilities with meeting drinking water standards.

In addition to parameters previously studied (Storlie, 2013), additional water quality and operational parameters need to be researched to gain a better understanding of the impact that water quality changes and operational conditions have on bromate formation. The previous MWTP bromate study quantified source water bromide concentrations, but limited samples were collected. There is a need to quantify the source water ammonia and to study the impact of ammonia concentration on inhibiting bromate formation because this has not been previously accomplished at the MWTP. Also, the previous MWTP study determined that total organic carbon may not be the best measurement to correlate organic concentration to bromate formation (Storlie, 2013). Therefore, parameters that may better explain the oxidation of organic matter during ozonation, such as ultraviolet absorbance at 254 nanometer wavelength (UV254), need to be studied to better determine the impact of organics oxidation and concentration on bromate formation. Additionally, the ability to monitor sectional operational parameters, such as ozone dose, was added as part of this study and will allow bromate formation to be studied on a section by section basis, as opposed to studying the ozone chamber as a whole.

1.1. Research Objectives

The main goals of this project are to determine the effectiveness of operational controls implemented to minimize bromate formation, and to gain a better understanding of how various water quality parameters and operational controls impact bromate formation so that the system operation may be improved. The objectives of this study include:

1) Conducting source water bromide analysis to verify source water selection strategies and conducting source water ammonia analysis to quantify the ammonia concentration in each source;
2) Developing and implementing operational changes and determining their effectiveness on minimizing bromate formation;

3) Studying the impact of specific water quality parameters not included in the previous bromate study, as well as previously studied parameters;
4) Providing an in-depth study of bromate formation in each ozone chamber section in relation to specific operational controls and water quality parameters; and
5) Verifying the current bromate prediction model or modifying it based on data collected after the implementation of operational changes.

Results from this study will provide MWTP with a more clear understanding of bromate formation during ozonation and help to determine if bromate formation can be minimized through operational changes. The results will also aid in the development of future operational strategies for the MWTP with regard to source water selection, ozone application, and disinfection calculations.

1.2. Scope of Work

Specific tasks were created in order to successfully complete the objectives of this research project. The specific tasks included: literature review, implementing operational changes in the MWTP, water sample collection and analysis, and verifying or modifying the current MWTP bromate prediction model.

A literature review was first conducted to gain an understanding of available information on bromate formation in ozonation processes like that at the MWTP. The literature being reviewed included journal articles, past theses and research manuals on the subject, and original design documents for the MWTP. The literature review was used to determine which objectives would be needed to meet the goals of this study. Past studies on bromate formation and disinfection by-product formation at the MWTP were reviewed in order to gain a better understanding of the MWTP ozonation process.

Operational changes were implemented at the MWTP at the beginning of this study to determine if bromate formation can be effectively minimized. The operational changes included discontinuing use of a groundwater source during the summer and maintaining better control of the ozonation system during disinfection. The effectiveness of these operational changes was evaluated by comparing bromate formation during this study to that of the previous study.

Water samples were collected during a seven month period from May to November 2013 to determine bromide and bromate concentrations. The MWTP source water was analyzed to determine if bromide data was consistent with that collected during the previous study and to quantify the source water ammonia concentration. Samples were also analyzed for other parameters found to be important to bromate formation including pH, temperature, DOC, UV254, and ammonia. The literature review, in-depth analysis of the MWTP treatment process, and results the previous study were used to determine important water quality parameters to be analyzed, as well as the sample locations for each parameter. Operational parameters found to impact bromate formation were recorded from the MWTP Supervisory Control and Data Acquisition (SCADA) system each time samples were collected.

Data collected from sample analysis was used to determine if the existing predictive bromate formation model presented by Storlie (2013) accurately predicted bromate formation in this study. The model was then modified to account for water quality changes resulting from the operational changes implemented. The purpose of modeling the data is to determine the impact each parameter has on bromate formation with relation to the other parameters analyzed. The goal of the modeling effort is to develop an accurate model that can be used to aid with operational control of the MWTP ozonation system.

CHAPTER 2. BACKGROUND

Based on extensive research on bromate toxicity and its formation in ozone disinfection processes, the United States Environmental Protection Agency (USEPA) mandated that regulations for bromate as a disinfection by-product (DBP) be developed (Miltner et al., 1992; Krasner et al., 1993). The regulatory process for the Stage 1 Disinfection/Disinfection By-Products (D/DBP) Rule formally began in 1992 and the bromate MCL was set at 10 ppb (Pontius & Diamond, 1999).

2.1. Bromate Formation Chemistry

Bromate formation in ozone disinfection processes is complex and depends on a variety of water quality parameters that are impacted by both the source water and water treatment plant conditions. Literature has described the reactions through which bromate forms in a variety of ways but, in general, the bromide ion is oxidized by either ozone or hydroxyl radicals and follows various pathways until the bromate formation reaction is complete (Galey et al., 2001; Symons & Zheng, 1997; Song et al., 1997). Table 1 presents chemical formulas for bromine species included in the three major bromate formation pathways: direct, direct-indirect, and indirect-direct. The formation pathways are described in Figure 1 and reaction equilibrium and kinetic parameters are shown in Table 2.

Table 1: Bromine species involved in bromate formation

Bromine Species	Chemical Formula
Bromide	Br^-
Hypobromite ion	BrO^-
Hypobromous acid	$HOBr$
Bromine oxide radical	$BrO^\bullet$
Bromite	BrO_2^-
Bromine radical	$Br^\bullet$
Bromate	BrO_3^-

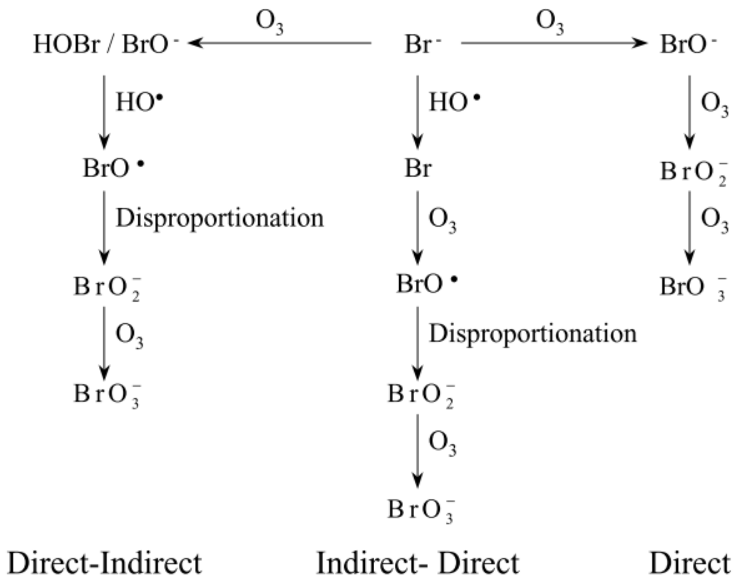


Figure 1: Bromate formation pathways (Song et al., 1997)

Table 2: Bromate formation reaction kinetics (adapted from Legube et al., 2004)

Pathway	Reaction	Rate (k) or equilibrium (pK_a) constant
	$HOBr \leftrightarrow BrO^- + H^+$	$K_a = 10^{-8.6}$
Direct	$O_3 + Br^- \rightarrow BrO^- + O_2$	$160\ M^{-1} \cdot s^{-1}$
	$O_3 + BrO^- \rightarrow Br^- + 2O_2$	$330\ M^{-1} \cdot s^{-1}$
	$O_3 + BrO^- \rightarrow BrO_2^- + O_2$	$100\ M^{-1} \cdot s^{-1}$
	$O_3 + BrO_2^- \rightarrow BrO_3^- + O_2$	$>10^5\ M^{-1} \cdot s^{-1}$
Direct-Indirect	$HO^{\bullet} + OBr^- \rightarrow BrO^{\bullet} + OH^-$	$4.5 \times 10^9\ M^{-1} \cdot s^{-1}$
	$HO^{\bullet} + HOBr \rightarrow BrO^{\bullet} + H_2O$	$2.0 \times 10^9\ M^{-1} \cdot s^{-1}$
	$2BrO^{\bullet} + H_2O \rightarrow BrO_2^- + BrO^- + 2H^+$	$4.9 \times 10^9\ M^{-1} \cdot s^{-1}$
Indirect-Direct	$Br^- + HO^{\bullet} \leftrightarrow BrOH^{\bullet -}$	$k = 10^{10}\ M^{-1} \cdot s^{-1}$
		$k' = 3.3 \times 10^7\ M^{-1} \cdot s^{-1}$
	$BrO^{\bullet -} \rightarrow Br^{\bullet} + OH^-$	$4.2 \times 10^6\ s^{-1}$
	$Br^{\bullet} + Br^- \rightarrow Br_2^{\bullet}$	$10^{10}\ M^{-1} \cdot s^{-1}$
	$Br_2^{\bullet} + BrO^- \rightarrow BrO^{\bullet} + 2Br^-$	$8.0 \times 10^7\ M^{-1} \cdot s^{-1}$
	$2BrO^{\bullet} + H_2O \rightarrow BrO_2^- + BrO^- + 2H^+$	$4.9 \times 10^9\ M^{-1} \cdot s^{-1}$
	$O_3 + BrO_2^- \rightarrow BrO_3^- + O_2$	$>10^5\ M^{-1} \cdot s^{-1}$

In the direct oxidation pathway, bromide (Br^-) is oxidized to bromate (BrO_3^-) by molecular ozone. Ozone oxidizes Br^- to form hypobromous acid/hypobromite ($HOBr/BrO^-$).

In this pathway, BrO^- (not HOBr) is the essential reactive bromine species and is oxidized by ozone to form bromite (BrO_2^-) and BrO_3^- (Song et al., 1997; von Gunten & Hoigne, 1994).

The remaining pathways involve oxidation by hydroxyl radicals ($HO^\bullet$) to form intermediate bromine species that are further oxidized by ozone to form bromate. The reaction rates for hydroxyl radical pathways are generally several orders of magnitude greater than for pathways utilizing ozone for oxidation (Williams et al., 2003). In the direct-indirect oxidation pathway, ozone oxidizes Br^- to BrO^-, which is then oxidized by the hydroxyl radical to form the bromine oxide radical ($BrO^\bullet$). Bromine oxide radicals react with water to form BrO_2^- and BrO^-. Bromite is then oxidized by ozone to form bromate. This reaction tends to be more favorable for bromate formation at higher pH values, when BrO^- is the dominant species over HOBr (Song et al., 1997; Haag & Hoigne, 1983; Siddiqui & Amy, 1993; Krasner et al., 1993).

In the indirect-direct oxidation pathway, bromide is oxidized by the hydroxyl radical to form $Br^\bullet$, which is then oxidized by ozone to form $BrO^\bullet$. Similar to the direct-indirect pathway, $BrO^\bullet$ converts to BrO_2^- and BrO^- through disproportionation reactions with water and BrO_2^- is then oxidized by ozone to form bromate (Song et al., 1997).

The formation pathway followed during ozonation is dependent on the characteristics of the water being treated. For example, the pH of the water will determine the $HOBr/BrO^-$ ratio in the water being treated and whether or not hydroxyl radicals form and are available to oxidize bromine species along each pathway involving indirect oxidation. In general, bromate control strategies must focus on minimizing concentrations of critical reactants (i.e. molecular ozone, hydroxyl radicals, and $HOBr/BrO^-$) in the water being treated (Song et al., 1997; Elovitz & von Gunten, 1999). This may be achieved by altering various water quality parameters or treatment processes.

2.2. Parameters Impacting Bromate Formation

As described in Section 2.1, bromate formation is complex and relies on a variety of water quality characteristics and operational parameters including bromide concentration, temperature, pH, organics content, ozone dose, ammonia concentration, and hydraulic residence time. Each parameter changes the amount of bromate that forms in an ozonation process or guides bromate formation down specific pathways. However, more than one of the variables is present in water at any given time. It is important to first understand how each water quality characteristic affects bromate formation individually before attempting to understand the simultaneous impact of multiple parameters. Each water quality characteristic has been extensively researched and their respective effect on bromate formation is explained in the following subsections.

2.2.1. Bromide

Bromate is not typically found in the natural environment, but is formed when ozone reacts with the bromide ion (Br^-), which is naturally occurring in geological formations or is from anthropogenic sources like mining and chemical production (Westerhoff et al., 1998; von Gunten, 2003; Jurenka, 2009). The amount of bromate that forms in ozone processes is positively correlated to the bromide concentration in water, meaning that the concentration of bromate increases with increasing concentrations of bromide at constant ozone doses (Galey et al., 2001; Song et al., 1997; Siddiqui & Amy, 1993). Song et al. (1997) determined that an average of 16.6 percent of the influent bromide concentration is converted to bromate, although conversion depends on raw water characteristics and water treatment processes including pH, ammonia, ozone dose, organics content, and initial bromide concentration. Maintaining bromate compliance with the Stage 1 D/DBP Rule may be achieved by ensuring the influent bromide concentration of the water is controlled.

2.2.2. Temperature

The amount of bromate formed during ozonation is also positively correlated to water temperature (Galey et al., 2001; Siddiqui & Amy, 1993; Legube et al., 2004). Galey et al. (2001) determined that bromate formation varied seasonally and found that increasing water temperature to greater than 15 degrees Celsius (°C) during summer months resulted in increased bromate formation. Another ozonation study showed that bromate formation increased by approximately 31 percent as the water temperature increased from 20 to 30°C (Siddiqui & Amy, 1993).

Water temperature impacts bromate formation because it affects reaction kinetics and the equilibrium constants of free bromine species involved in bromate formation. The dissociation constant (K_a) of $HOBr/BrO^-$ is highly temperature dependent, as the K_a varies from $10^{-8.91}$, $10^{-8.66}$, to $10^{-8.49}$ for the temperatures of 10, 25, and 35°C, respectively (Arvai et al., 2012). The increase of dissociation constant at higher temperatures increases the BrO^- concentration available to be oxidized by ozone if the pH is held constant throughout the temperature range (Legube et al., 2004).

Water temperature also affects ozone decay rates by changing its half-life and the concentration of ozone that needs to be applied to meet disinfection requirements, as ozone depletion rates increase with increasing temperature. Ozone depletion has been determined to be first-order, with ozone decay rates increasing approximately 18-fold over the temperature range of 5 to 35°C. As water temperature increases, ozone becomes more reactive and its half-life is reduced, resulting in decreased ozone exposure at constant ozone doses. However, $HO^\bullet$ exposure remains constant throughout normal water treatment temperature ranges because it does not form in easily measureable quantities (Elovitz et al., 2000). The decrease in ozone exposure at higher temperatures requires higher ozone doses to achieve disinfection, which may increase bromate formation as a result.

2.2.3. pH

The relationship of pH with $HOBr/BrO^-$ equilibrium, hydroxyl radical formation, and ozone dose required for disinfection greatly impacts bromate formaiton (Siddiqui & Amy, 1993; Krasner et al., 1993; Galey et al., 2001; Westerhoff et al., 1998). In general, bromate formation increases with increasing pH (Williams et al., 2003; Song et al., 1997; Westerhoff et al., 1998).

In the direct formation pathway involving $HOBr/BrO^-$, bromate formation requires oxidation of BrO^-, as it is the reactive species with dissolved ozone. Knowing that BrO^- is the dominant $HOBr/BrO^-$ species at higher pH (Figure 2) suggests that bromate formation will increase with increasing pH (Williams et al., 2003; Krasner et al., 1993; von Gunten, 2003). Increasing the pH of water will also lead to faster ozone decomposition rates, resulting in increased hydroxyl radical formation (Langlais et al., 1991; Elovitz et al., 2000). The hydroxyl radical is a more powerful oxidant than molecular ozone and increasing its concentration can increase the formation potential of bromate (von Gunten & Hoigne, 1994). At pH values below the dissociation constant, HOBr dominates and may react with natural organic matter to form brominated organic compounds (Arvai et al., 2012). Also, less HOBr is oxidized to form bromate because hydroxyl radical formation is decreased at lower pH values.

Reducing the pH of the water being ozonated has proven to be an effective bromate control strategy in multiple studies (Williams et al., 2003; von Gunten, 2003; Neemann et al., 2004). In a study by Galey et al. (2000), pH depression was determined to be the best operational control used to minimize bromate formation in full-scale systems. Increasing the pH from 6.0 to 7.5 increased bromate formation by nearly 25 ppb, which is significant considering the bromate MCL is 10 ppb (Galey et al., 2001). In another study, increasing the pH from 6.0 to 8.5 resulted in an increase of approximately 20 ppb bromate due to a shift from molecular ozone to hydroxyl radical oxidation. Also, the concentration of bromide required to form bromate has been shown to decrease as pH increases (Siddiqui & Amy, 1993). However, the literature reviewed evaluated bromate formation at pH values of approximately 6.0 to 9.0 (Elovitz et al., 2000; Siddiqui & Amy, 1993; Neemann et al., 2004; Galey et al., 2000; Galey et al., 2001; Williams et al., 2003; von Gunten, 2003), which is less than the normal ozonation pH at MWTP. This study is required to provide more information on bromate formation at higher pH values.

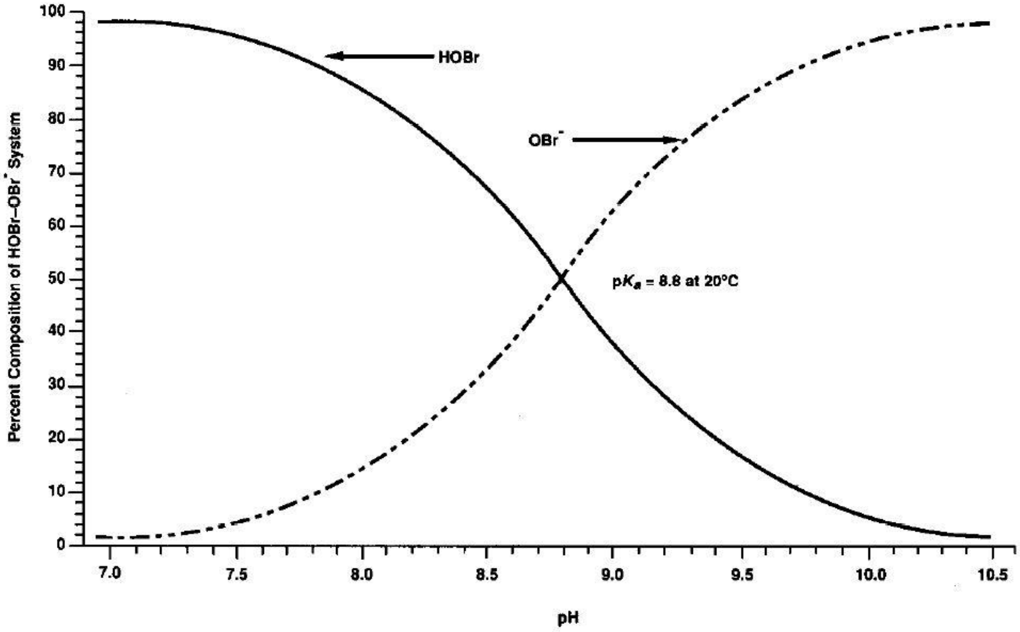


Figure 2: Distribution of HOBr/BrO$^-$ in aqueous solutions (Krasner et al., 1993)

2.2.4. Organics

The relationship of organics content and bromate formation is complex, as organics may consume ozone that would be available to oxidize bromide; however, increased organics content may also require higher ozone doses to meet disinfection requirements. Westerhoff et al. (1998) found that the presence of NOM in water during ozonation always caused decreased bromate formation when compared to an equivalent water not containing NOM. Other studies have also shown that as the organics content increases, the amount of bromate formation decreases (Song et al., 1997; Siddiqui & Amy, 1993).

Bromide competes with NOM in reactions with ozone and $HO^\bullet$ because NOM also exerts a demand for the oxidants. It has been determined through a bench-scale kinetic competition study that ozone reacts more readily with NOM than with Br^-, and that $HO^\bullet$ reacts more readily with NOM than with $HOBr/BrO^-$ (Westerhoff et al., 1998). Also, NOM reacts with $HOBr/BrO^-$ to form organobromines (TOBr) more quickly than ozone reacts with BrO, which may result in less free bromine being available to be oxidized to form bromate, as shown in the equation below (Westerhoff et al., 1998; Song et al., 1997).

$$HOBr/BrO^- + NOM \leftrightarrow TOBr$$

Total organic carbon (TOC) and dissolved organic carbon (DOC) are measurements of the organic content in water. Studies have shown that the amount of TOC or DOC does not change significantly throughout ozonation (Guo et al., 2007; Storlie, 2013). However, biodegradable dissolved organic carbon concentrations have been found to increase at higher ozone dosages (Miltner et al., 1992), which suggests that ozone may not completely mineralize organics but breaks them down before oxidizing bromide. Unless complete mineralization occurs, the total organic carbon (TOC) concentration of water will not change greatly during ozonation (Miltner et al., 1992).

Ultraviolet absorbance at a wavelength of 254 nanometers (UV254) is a measurement of the UV-absorbing compounds in water. Aromatic carbon double bonds absorb UV light, and UV254 is often used to measure these compounds in water samples. Measurement of the influent and effluent UV254 can be used to determine partial oxidation or destruction of aromatic NOM during ozonation. It has been determined that the reduction of UV-absorbing compounds increases with increasing ozone doses (Miltner et al., 1992). When ozone reacts with aromatic carbons in water, low-molecular weight compounds, called ozone by-products, are formed and TOC/DOC may be converted to BDOC (Miltner et al., 1992; Siddiqui & Amy, 1993). At low ozone-to-TOC ratios less bromate forms than at high ozone-to-TOC ratios, suggesting that ozone reacts more readily with organics than with bromide (Miltner et al., 1992; Song et al., 1997). Westerhoff et al. (1998) found that consumption of ozone by NOM clearly dominated bromide oxidation by an order of magnitude.

2.2.5. Ozone Dose

The ozone dose applied to water has been found to be positively correlated to bromate formation (Galey et al., 2001; Guo et al., 2007; Song et al., 1997). In a study by Miltner et al. (1992), no changes in bromide concentration were determined at ozone doses less than 1 mg O_3 per mg TOC, but bromide was converted to bromate at higher ozone doses. Other studies have found that bromate formation is directly related to the amount of ozone dosed or consumed (Siddiqui & Amy, 1993; Westerhoff et al., 1998). In a study by Guo et al. (2007), increasing ozone dose from 2.0 to 2.8 mg/L resulted in bromate formation increasing from 5 to 12.5 ppb. Galey et al. (2004) found that when the ozone dose was increased from 0.85 to 3.5 mg/L the bromate concentration increased from less than 2 to nearly 15 ppb. Using the minimum ozone dose required to achieve disinfection has been recommended as a method to reduce bromate formation (Galey et al., 2001; Song et al., 1997).

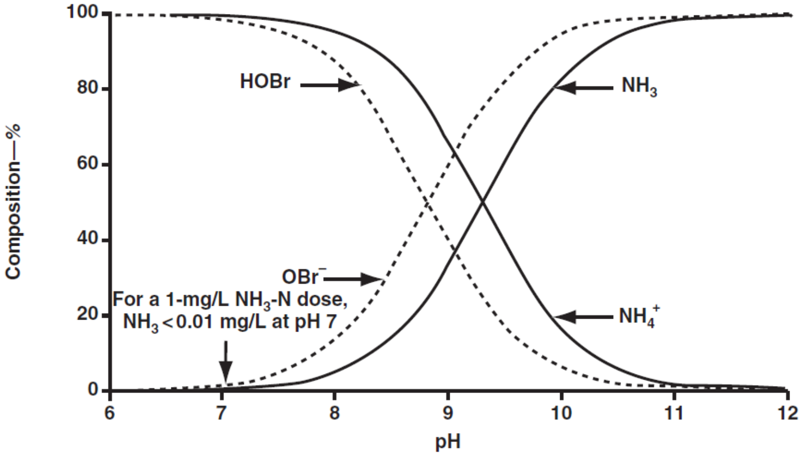
2.2.6. Ammonia

Bromate formation has been found to be negatively correlated to ammonia concentration (Galey et al., 2001; Westerhoff et al., 1998; Song et al., 1997). When ammonia is naturally present or is added in a treatment process it reacts with aqueous bromine ($HOBr/BrO^-$) to form bromamines following the reaction below (Song et al., 1997; Williams et al., 2003; Hofmann & Andrews, 2007; von Gunten, 2003; AWWA & ASCE, 2012).

$$NH_3 + HOBr \rightarrow NH_2Br + H_2O$$

This reaction prohibits bromate formation because it consumes $HOBr/BrO^-$ to form monobromamine faster than does ozone (Siddiqui & Amy, 1993; Krasner et al., 1993; Neemann et al., 2004). Monobromamine formation is due to reactions between the nonionic species of ammonia and free bromine at pH values less than 11.0, with BrO^- being approximately 2,000 times less reactive with ammonia than HOBr (Hofmann, 2000;

Hofmann & Andrews, 2001). The optimal pH for bromamine formation in water has been determined to be 9.0 by averaging the pK values at 20°C of HOBr (pK=8.7) and NH_3 (pK=9.3), as shown in Figure 3 (Williams et al., 2003).



HOBr—hypobromous acid, NH_3—ammonia, NH_4^+—ammonium ion, OBr^-—hypobromite ion

Figure 3: Ammonia and bromine speciation as a function of pH (Williams et al., 2003)

Ammonia has been found to reduce bromate formation when it is applied pre-ozonation. Siddiqui and Amy (1993) reduced bromate formation by approximatley 36 percent by adding ammonia pre-ozonation. Another study found dosing 0.5 mg/L ammonia prior to ozonation reduced bromate formation from 20 to 25 ppb down to approximately 5 ppb (Neemann et al., 2004). A one-to-one (ammonia-to-bromide) molar ratio has resulted in average reductions in bromate formation between 40 and 50 percent (Song et al., 1997; Glaze et al., 1993). However, if bromate formation is predominantly through the indirect-direct pathway, where HOBr/BrO^- is not involved, ammonia addition will not help to decrease bromate formation (Song et al., 1997).

2.3. Moorhead Water Treatment Plant

Located in Moorhead, Minnesota, the Moorhead Public Service (MPS) water treatment facility serves the cities of Moorhead and Dilworth, as well as Oakport Township. Approximately 12,000 metered connections in Moorhead's water system serve an estimated population of 44,000 people (Moorhead Public Service, 2013). MPS has the capacity to treat

16 MGD through two water treatment plants, which are located on the same property. However, the older of the two facilities, which was built in 1961 and has a 6 MGD capacity, has not been used since the newer facility (10 MGD) was completed and put online in February 1995. The 1961 plant is not currently used and would take an entire team of operators multiple days to get it in running condition. However, in the event of an emergency or complete failure of the new plant the old plant would be put into operation. The 1995 plant utilizes lime-softening, ozone disinfection, dual-media filtration, and secondary disinfection with chloramines to treat both surface water from the Red River of the North (Red River) and groundwater from two aquifer sources. This study focused on the 1995 plant, hereafter referred to as the Moorhead Water Treatment Plant (MWTP).

The average monthly water demand patterns in the MWTP service area between 2003 and 2013 are shown in Figure 4. In the past decade, water use in Moorhead has followed a similar pattern in that the summer demand averages above 4.5 MGD and winter demand remains at about 4.0 MGD. Between 2003 and 2013, the average monthly demand for the MWTP was 4.38 MGD. The peak monthly demand during that time period was 7.63 MGD (July 2006), and the minimum monthly demand was 2.86 MGD (March 2009 and December 2010). In 2013, MWTP's peak demand was 7.02 MGD and the minimum demand was 3.27 MGD; the average demand for 2013 was 4.23 MGD.

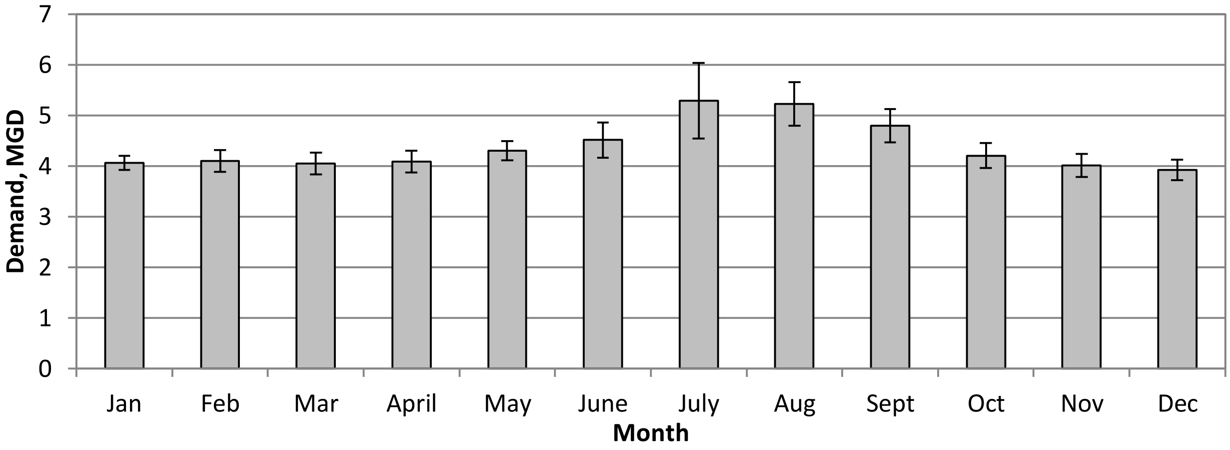


Figure 4: MWTP average monthly water demands (2003-2013)

2.3.1. Water Sources

The MWTP treats both surface water and groundwater to meet the municipal and industrial demands of the service area. When water quality permits the MWTP treats water solely from the Red River. Groundwater is used as a supplemental water source, most often during the summer, to reduce the temperature of the finished water or to combat unfavorable water quality conditions in the Red River. Since 1997, 81.1 percent of the water treated by the MWTP has been withdrawn from the Red River to conserve groundwater resources in the event of a major drought or contamination of the Red River that would require groundwater to be the primary water source. The daily flow of water from MWTP's different sources in 2013 is illustrated in Figure 5. Decant water from MWTP's lime-sludge ponds is also used as a supplemental source.

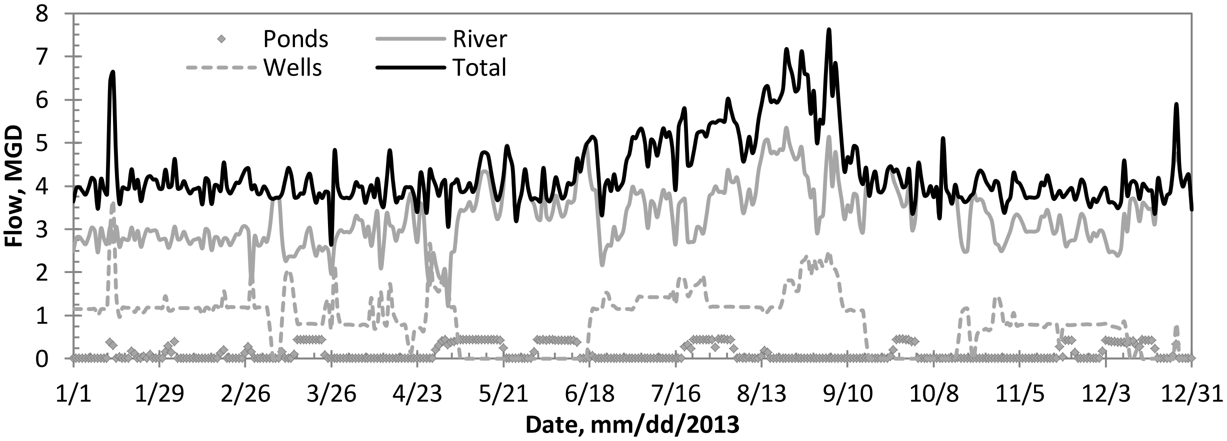


Figure 5: MWTP daily plant flow (2013)

2.3.1.1. Red River of the North

The Red River of the North (Red River) originates near the cities of Wahpeton, North Dakota and Breckenridge, Minnesota at the confluence of the Bois de Sioux and Otter Tail Rivers. From there it flows north and forms the border between Minnesota and North Dakota until it reaches the Canadian border, eventually draining into Lake Winnipeg in Manitoba, Canada. As a surface water body, water quality parameters like temperature, turbidity, organics content, hardness, and alkalinity in the Red River fluctuate between seasons; daily or even hourly changes in water quality are not uncommon. These fluctuations in water quality can change rapidly due to natural influences, such as air temperature and precipitation, and make treating the Red River very challenging.

Water temperature and turbidity remain relatively constant in the winter months when the Red River is frozen over and not exposed to the atmosphere. After ice melts in the spring and snow melt begins to run off into the river, the water temperature and turbidity begin to change rapidly, as illustrated in Figure 6. The turbidity can increase to over 600 NTU during spring runoff and rain events and the water temperature rises to nearly 80 degrees Fahrenheit (°F) during the summer. The MWTP uses well water to combat spikes in turbidity and to reduce the temperature of the finished water to below 72°F, as requested by Moorhead's largest industrial water customer.

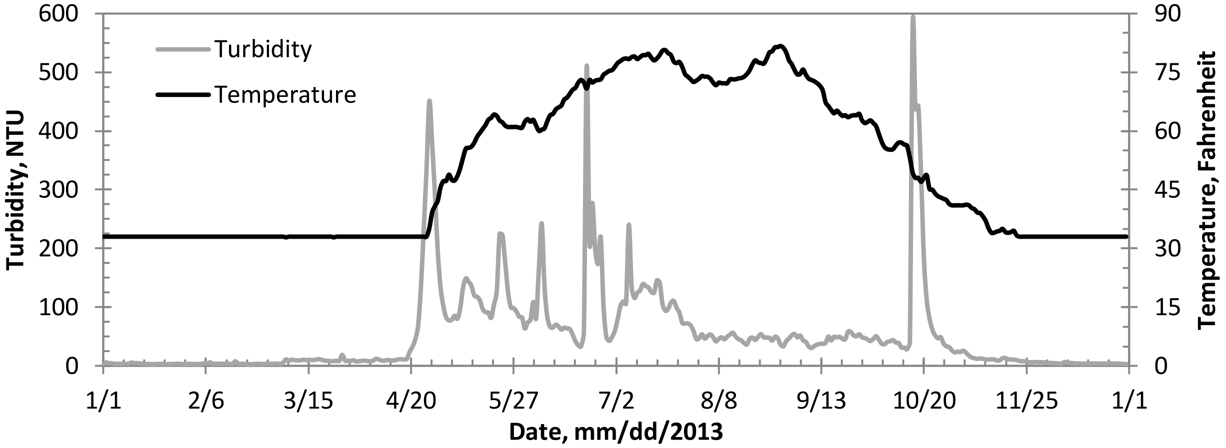


Figure 6: Red River water temperature and turbidity

Total organic carbon (TOC) is a water quality characteristic that the MWTP monitors to determine the organics content in the Red River. The MWTP may increase the well water percentage as the Red River TOC increases because the increased organics content can cause taste and odor problems, increased chemical usage, and difficulty meeting USEPA disinfection requirements that are described in Section 2.4.2. Between 2007 and 2012 the monthly TOC average ranged from 7.7 to 13.1 mg/L. The Red River TOC may change for a variety of reasons, including spring floods, snowmelt, or storm water runoff that conveys organics into river, and leaves or other organic matter decomposing in the river during the fall. Upstream discharges from industry or wastewater treatment facilities may also affect the Red River water quality. An example of rapid TOC change can be seen in March 2009, when the Red River experienced record flood levels and the TOC increased from 8.5 to 12.0 mg/L over a two-week period, as shown in Figure 7 (Portlock, 2012).

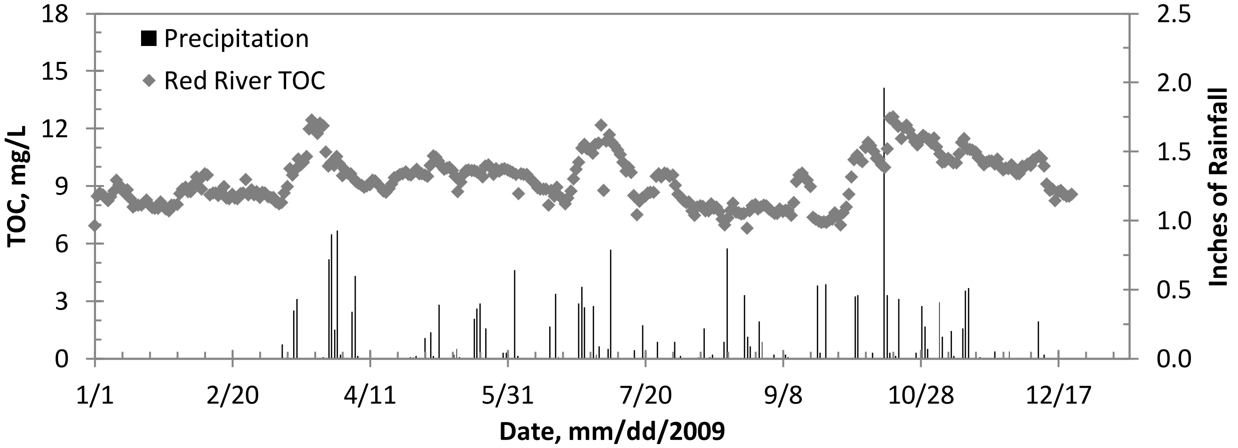


Figure 7: 2009 Red River daily TOC (adapted from Portlock, 2012)

Construction of a new Red River pumping station and intake screen was completed in July 2013 to replace a pumping station that was prone to flooding and utilized equipment that had surpassed its useful life. The new pumping station has many operational advantages for the MWTP. The new pumps are equipped with variable frequency drives so water flow into the plant can be controlled more effectively. Also, the river intake was moved from the river bank to the center of the river channel. Changing the intake location helps with operation of the MWTP ozone disinfection system. In the past during a rainstorm, runoff flowing out of a storm water outfall just upstream of the intake would travel along the riverbank and be pumped into the MWTP before it could disperse into the Red River. The increased organics load in the runoff often caused the ozone residual to drop below that required by the USEPA if the ozone dose was not increased quickly enough. It is expected that relocating the intake helped alleviate this problem and has allowed for more consistent operation of the ozone system.

2.3.1.2. Groundwater

The MWTP pumps groundwater from seven wells in two aquifers, the Moorhead Aquifer and Buffalo Aquifer, as shown in Figure 8. It should be noted that there are two different well fields in the Buffalo Aquifer; North Buffalo and South Buffalo.

Two of the wells (6 and 6B) are located in the Moorhead Aquifer and are across the street from the MWTP. The other five wells pump water from the Buffalo Aquifer; two (1 and 2) are in the North Buffalo well field which is northeast of Moorhead and three (8, 9, and 10) are in the South Buffalo well field. Some important characteristics of each well are presented in Table 3.

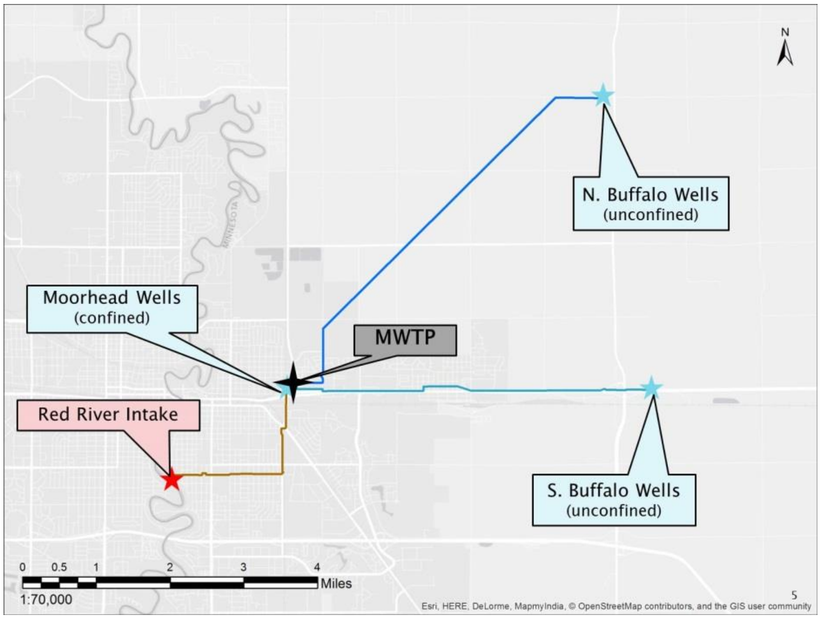


Figure 8: MWTP source water locations

The Moorhead Aquifer is located within the city limits of Moorhead and was used as a water source as early as the 1900s. A layer of low permeability clay creates a protective barrier between the surface and water in the aquifer. Because of this barrier, there is no known connection between surface water and the water within the formation and natural groundwater recharge does not occur through infiltration. Oxygen isotope samples from the well estimate water in the aquifer could be more than one-thousand years old (Soule, 2012). Very little else is known about the origin of water, or the cause of certain water quality parameters, contained in the Moorhead Aquifer. When the Red River's hardness increased to more than 500-600 mg/L as $CaCO_3$, the MWTP used the Moorhead wells (6 and 6B) to reduce the total hardness in the plant's influent. Since the Moorhead Aquifer is the softest water source, using it when the Red River is very hard reduces the chemical costs required to soften the water.

Table 3: Moorhead groundwater source characteristics

Aquifer	Well No.	Unique Well No.	Depth (ft)	Capacity (MGD)	Hardness (mg/L)	TOC (mg/L)
North Buffalo	1	511085	190	1.53	516	1.62
	2	511086	203	1.21	516	1.59
South Buffalo	8	222049	116	1.15	464	1.75
	9	222050	114	1.43	396	2.00
	10	222051	124	2.74	396	N/A
Moorhead	6	241492	273	0.65	188	2.09
	6B	437645	266	0.79	188	2.00

N/A – not available

The Buffalo Aquifer, which is located east of Moorhead, has a north-south length of about 32 miles, and ranges between one and eight miles in width (east-west). Water flows from south to north in the aquifer as the water surface elevation decreases from about 955 feet in the south end to 880 feet in the north end. Unlike the Moorhead Aquifer, the Buffalo Aquifer is unconfined and water levels can be as high as 15 feet below ground surface (Moorhead Public Service, 2013). Since the new MWTP came online in 1995, static water levels in the Buffalo Aquifer wells have risen nearly 20 feet (Figure 9) because the Red River became the primary water source and groundwater is used as a supplemental source. The North Buffalo well field was constructed in 1988 to increase the groundwater capacity that could be treated. Previously, well water was pumped in greater volumes to be treated in the old water treatment plant. The Buffalo Aquifer wells have higher yields than the Moorhead Aquifer wells, so they are used when groundwater capacity needs to be added to the total flow being treated.

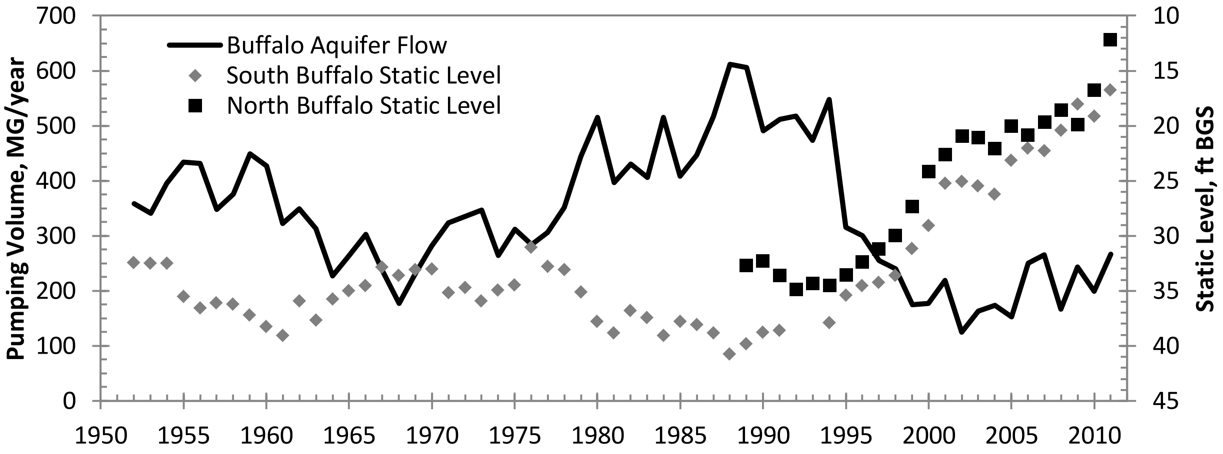


Figure 9: Buffalo Aquifer annual pumping volume and static water levels (1950-2012)

Well water is used to combat changing water quality in the Red River. Water quality parameters including turbidity, temperature and TOC may be controlled using a combination of groundwater and the Red River. Well water has a fairly constant temperature (48 to 5°F) and is used to reduce the finished water temperature because MPS' largest industrial customer prefers the finished water temperature to be below 72°F (Figure 10).

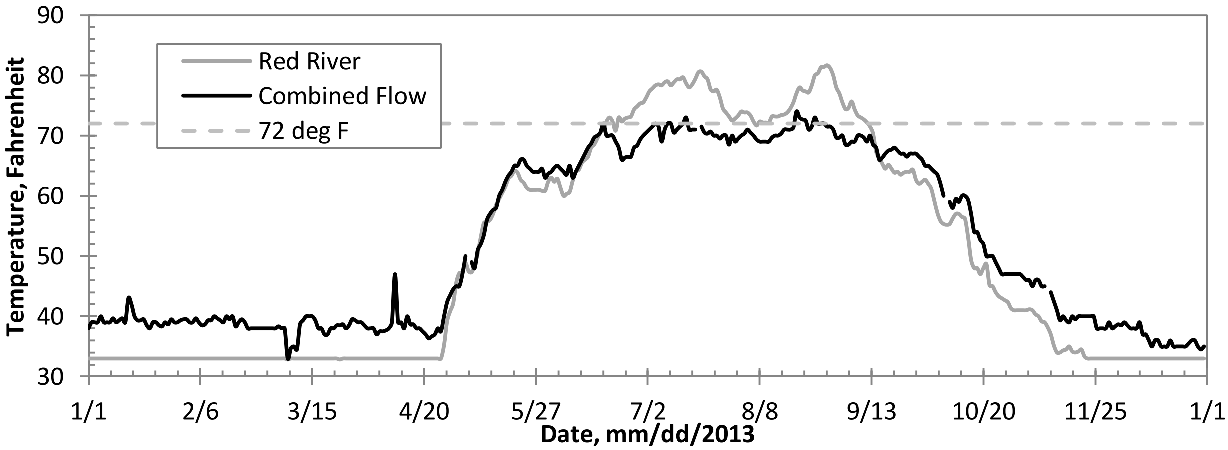


Figure 10: MWTP water temperature

As described, the MWTP also uses well water to reduce the plant influent TOC to aid with the ozone system operation; high levels of TOC can make it difficult to maintain the required CT in the ozone system to meet disinfection requirements. The reduction in TOC that is achieved by combining river water and well water, which is usually in the range of one to three milligrams per liter, is shown in Figure 11.

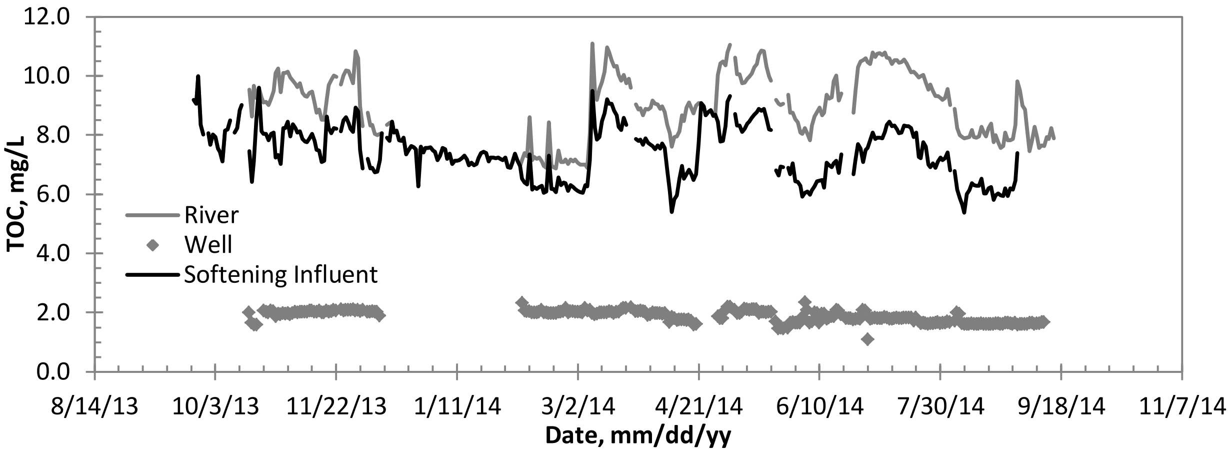


Figure 11: Raw water TOC compared to softening influent TOC

2.3.2. Water Treatment Process

Treatment processes used in the MWTP include lime/soda ash softening, ozonation for primary disinfection, dual-media biological filtration, and addition of chloramines for secondary disinfection. The MWTP process flow diagram is shown in Figure 12. Chemical feed points are denoted by black squares labeled 1 to 11. When water enters the plant through the Red River and groundwater influent pipes it is mixed in the inlet structure. Ferric sulfate ($Fe_2(SO_4)_3$), which is used as a coagulant, is injected into the Red River influent pipe and a flash mix pump is used to aid with mixing in the pipe. The influent channel gives raw water additional time to react with ferric sulfate before flowing by gravity into the softening basins.

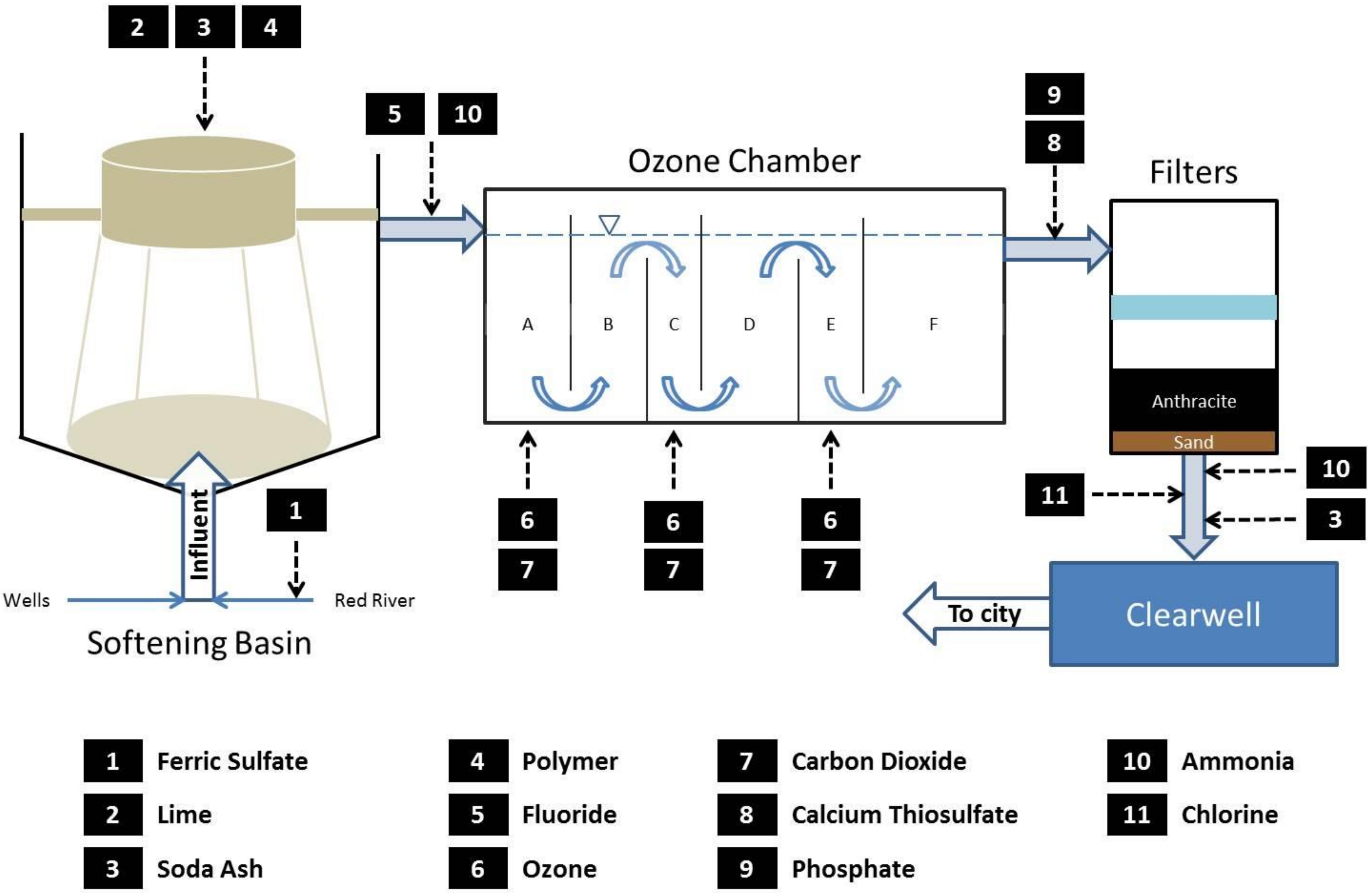


Figure 12: MWTP process flow diagram

2.3.2.1. Lime/soda ash softening

The lime/soda ash softening process employed at the MWTP involves removing hardness-causing minerals, mainly calcium and magnesium, using lime (calcium hydroxide, $Ca(OH)_2$) and soda ash (sodium carbonate, Na_2CO_3). In this process, the pH is maintained above 10.6 so magnesium hydroxide precipitates out of the water. Lime removes carbonate hardness while soda ash removes non-carbonate hardness. The MWTP removes hardness to a level of approximately 100 mg/L as calcium carbonate (mg/L as $CaCO_3$). The MWTP has two softening basins, which have a design volume of about 336,000 gallons each and dimensions of 50 feet long by 50 feet wide and about 18 feet deep. Each basin is designed to treat 5.5 MGD. Most of the time only one basin is used, but when flows are greater than 5 MGD for extended periods of time, most often during summer months, two softening basins are used to treat the increased flows.

Each softening basin contains an Infilco-Degremont Accelator® solids contact clarifier, which utilizes internal sludge recirculation to accelerate chemical reactions and create a dense floc that settles to the bottom of the basin. Lime and soda ash are added to the center of the Accelator®, where a low-speed impeller mixes the chemicals and creates floc particles that form a sludge blanket. An anionic polymer is also added to thicken the sludge and aid in floc settlement. A rake attached to the hood of the Accelator® helps circulate the sludge blanket and move it into pits where it is periodically pumped to lime-sludge ponds.

Although the primary purpose of this treatment stage is softening and clarification, some disinfection credits are also earned. The MWTP is required to achieve 3-log *Giardia* and 4-log virus removal throughout its treatment process by the Minnesota Department of Health (MDH). The softening process is awarded 2.5-log *Giardia* and 2-log virus removal credit, leaving 0.5-log *Giardia* and 2-log virus inactivation remaining to be achieved through primary and secondary disinfection processes.

The MWTP is also required to monitor TOC and alkalinity throughout the treatment process by the Stage 1 D/DBP Rule, which requires conventional surface water systems to achieve certain TOC removal, based on the raw water alkalinity and TOC, in order to remove DBP precursors. The amount of TOC typically removed in the MWTP softening process is shown in Figure 13; on average, about 45 to 50 percent of the raw water TOC is removed. For reference, the MWTP is most often required to remove roughly 25 to 30 percent of the TOC in the plant's raw water based on the Stage 1 D/DBP Rule requirements, as determined by Table 4. However, the removal requirement may change based on the raw water quality at the time of sampling.

Treated water from the softening basins flows upward into launders before flowing into the ozonation influent channel containing the combined flow from both basins, if both are in use. Fluoride is added in the ozone chamber influent before water flows into the ozone chamber for primary disinfection. Ammonia addition is optional in the effluent launder, with the goal of preventing bromate formation in the ozonation chamber.

Table 4: Stage 1 D/DBP Rule required TOC removal (adapted from USEPA, 2001)

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

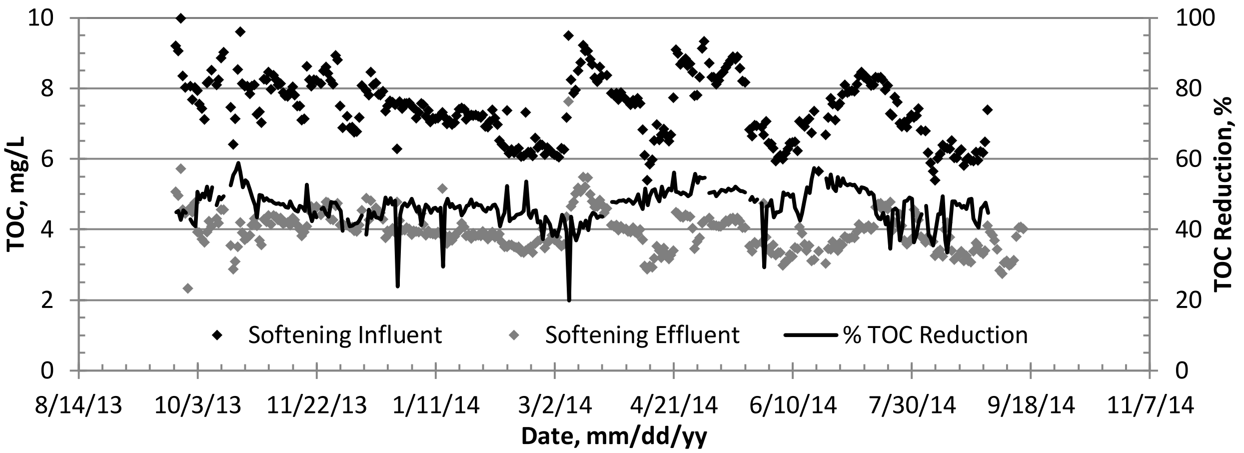


Figure 13: Softening basin influent and effluent TOC comparison

2.3.2.2. Ozonation and Recarbonation Chamber

The ozonation and recarbonation chambers (ozone contact chambers) at the MWTP are operated to achieve three objectives: taste and odor control, recarbonation, and primary disinfection. The MWTP generates ozone on-site for organics oxidation and disinfection but receives chemical deliveries of carbon dioxide for recarbonation and stores it on-site. Ozone is generated on-site in a two-step process: feed gas preparation and ozone generation. A pressure swing adsorption (PSA) system produces approximately 95 percent pure oxygen to be used as a feed gas for the ozone generators. This is accomplished by passing air through an adsorbent bed that preferentially adsorbs nitrogen from the air, leaving nearly pure oxygen in the feed gas. Ozone is generated when oxygen from the PSA system passes through corona discharge that forms in the gap between two electrodes inside the ozone generators, one of which is coated with a dielectric material (AWWA & ASCE, 2012). Approximately three to six percent of the oxygen gas passing through an ozone generator is converted from oxygen to ozone. The ozone is then fed through fine-bubble diffusers into the water in the ozonation chambers. Carbon dioxide is also applied for recarbonation through the same type of diffusers.

Each of the MWTP's ozonation chambers is designed with a capacity of 5 MGD. When plant flow is less than 5 MGD, only one ozone chamber is used; if plant flow is greater than

5 MGD, flow is split equally between the two ozonation chambers. The ozonation chamber is split into six cells (A-F), but, for the purposes of this study, the cells were paired to form three sections (1-3). The volume and design hydraulic retention time (HRT) of each section is described in Table 5. Ozone (O_3) is applied to the water in Cells A, C, and E and sample taps are located at the effluent of Cells B, D, and F to measure the ozone residual. A diagram of a MWTP ozone chamber is illustrated in Figure 14.

Table 5: Ozone chamber details (JMM Consulting Engineers, Inc., 1992)

Section	Volume (gal)	Design (5 MGD) HRT (min)
1	28,700	8.3
2	26,800	7.7
3	36,300	10.5

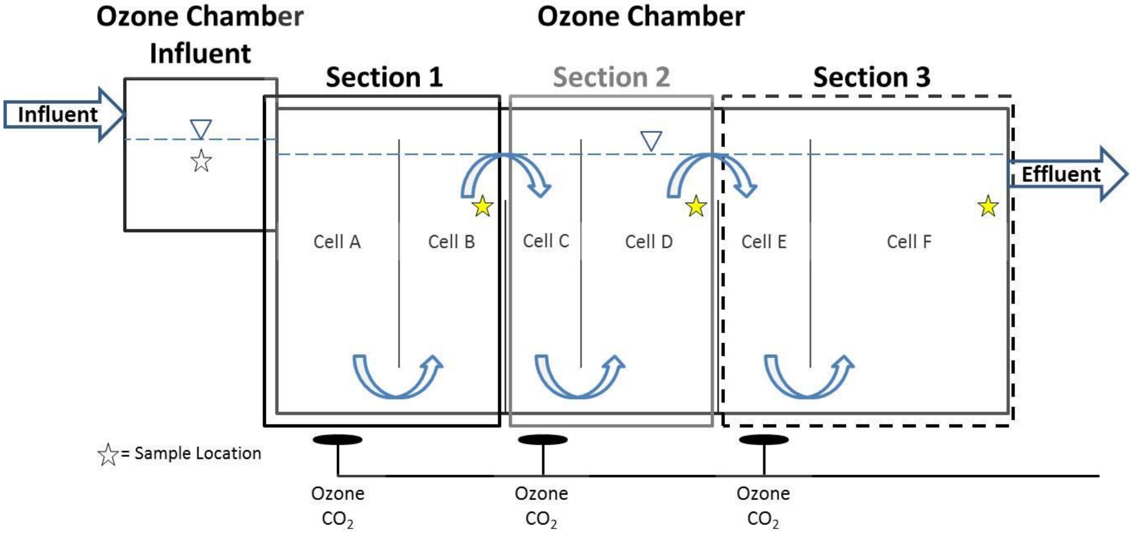


Figure 14: MWTP ozone chamber schematic

Taste and Odor Control

The MWTP was originally designed to employ an advanced oxidation process (AOP) in Section 1 of the ozone chamber by applying ozone to water at a pH of greater than 9.50 to produce hydroxyl radicals. The purpose of this was to more effectively oxidize organics and taste and odor compounds that are often found in surface waters. However, when bromate formation became a concern in the early 2000s, a carbon dioxide feed point was added in

Section 1 to reduce the ozonation pH earlier in the process during the summer. It is possible that taste and odor control is not as effective when the ozone system is operated in this manner because less $HO^{\bullet}$ is formed at lower pH values, although MWTP has not determined that this is an issue.

Hydroxyl radicals ($HO^{\bullet}$) are formed most efficiently when ozone is applied to water at a pH greater than 7.0 (Rakness, 2005). Typically, water entering the MWTP ozone chamber has a pH of greater than 10.6, favoring $HO^{\bullet}$ formation. However, hydroxyl radicals have a half-life in the range of microseconds and it is not possible to maintain high concentrations. The formation of $HO^{\bullet}$ is beneficial because it is a nonselective oxidant and will react with nearly all compounds. When compared to other oxidants like ozone and chlorine, the hydroxyl radical has an electrochemical oxidation potential (EOP) of 1.35 times greater than ozone and 2.05 times greater than chlorine (AWWA & ASCE, 2012).

Although Section 1 is used to oxidize organics remaining in the water after the softening process, most organics are not entirely reduced to carbon dioxide. A previous MWTP study determined that TOC is not greatly removed during ozonation, but UV254 is reduced by more than 50 percent (Storlie, 2013). This finding suggests that unsaturated organics containing carbon-carbon double bonds or triple bonds are partially oxidized broken down to short chain compounds that are more readily biodegradable and removal through biological processes. However, some mineralization of organic matter does take place during ozonation. TOC reduction in the ozone chamber is usually less than ten percent, or between 0.1 and 0.4 mg/L (Figure 15). Based on 2013-2014 MWTP data, more TOC reduction is achieved during the summer when the water temperature is higher. The average TOC reduction in the MWTP ozone chamber from October 2013 to September 2014 was 0.3 mg/L (6.7 percent).

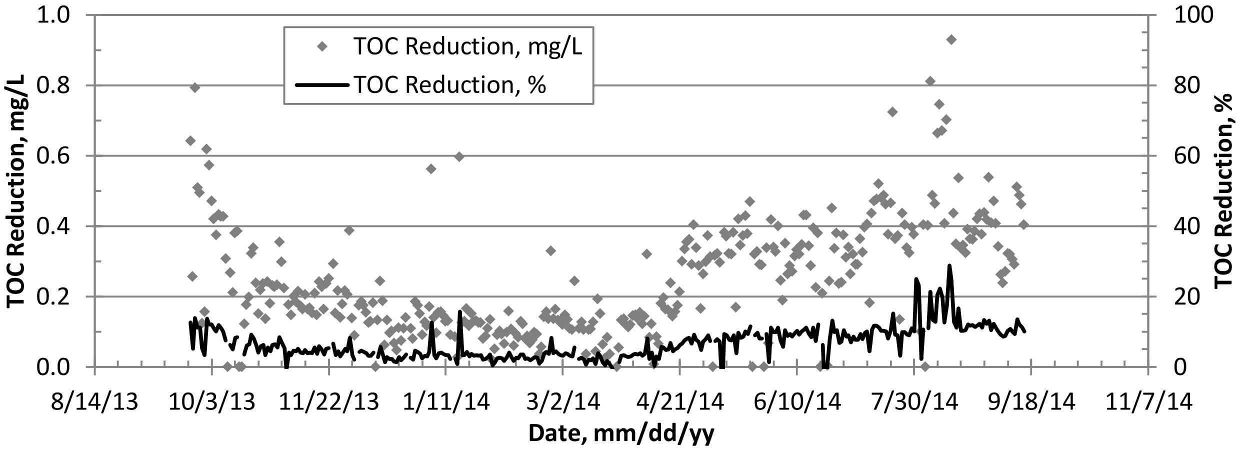


Figure 15: Ozone chamber TOC reduction

Recarbonation

Carbon dioxide (CO_2) is applied in Cell A or Cell C to drop the pH from greater than 10.6 to approximately 9.30. MWTP can also feed CO_2 in Cell E; however, this is rarely practiced. Originally, the MWTP was designed to feed CO_2 in only Cell C or Cell E so Section 1 could be used for taste and odor control, but the process was modified in July 2002 to allow for CO_2 feed in Cell A after bromate formation during the summer months became a concern.

Since the recarbonation system was modified, the ozonation chamber has been operated differently between seasons. During the winter, fall, and spring CO_2 is applied in Cell C so Section 1 may be used for its original purpose, taste and odor control. Since bromate formation is dependent on water temperature, MWTP has not been concerned with bromate forming higher than the MCL during the winter. During the summer, the CO_2 feed point is switched to Cell A so the ozonation pH is reduced earlier in the process, as it is also known that bromate formation increases at higher pH values. After recarbonation, the ozone contact chamber is used for primary disinfection.

Primary Disinfection

As stated previously, the MWTP is required to remove 3-log *Giardia* and 4-log virus. The MDH has granted the MWTP softening process 2.5-log *Giardia* and 2-log virus removal, leaving 0.5-log *Giardia* and 2-log virus inactivation remaining to be achieved through ozone disinfection. The USEPA has developed a required CT (CT=disinfectant concentration x contact time) based on water temperature for ozone disinfection in water treatment. Table 6 shows the required CT values for inactivation of *Giardia* and viruses by ozone (USEPA, 1999). The level of disinfection that must be achieved at various temperatures based on Table 6 is more easily seen when the values are plotted in Figure 16.

Table 6: CT values for *Giardia* and virus inactivation by ozone (USEPA, 1999)

Temperature	1	5	10	15	20	25
0.5-log Giardia	0.48	0.32	0.23	0.16	0.12	0.08
2.0-log Viruses	0.9	0.6	0.5	0.3	0.25	0.15

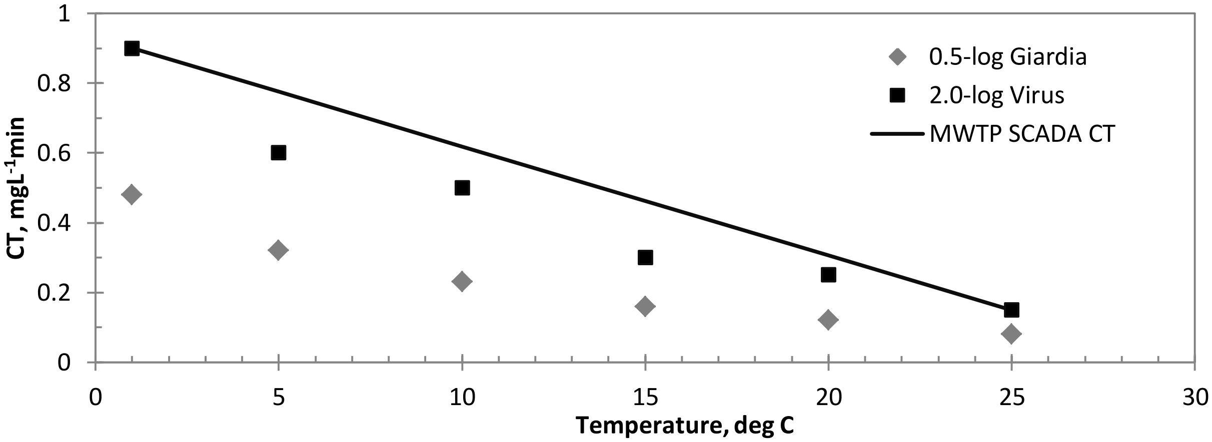


Figure 16: MWTP SCADA CT and USEPA required CT

According to Figure 16, 2-log virus inactivation is the controlling factor for disinfection, as it requires a higher CT than 0.5-log *Giardia* inactivation. To ensure disinfection compliance 100 percent of the time, a CT equation was programmed into the SCADA system by first developing a 2-log virus removal equation using the first and last points from the USEPA CT tables. Connecting these points gives a conservative and linear representation of the required CT for 2-log virus inactivation. The resulting equation allows disinfection in the ozone chamber to be monitored and adjusted by comparing the required CT to the actual CT calculated in the ozone chamber. The amount of ozone being applied to water is based on the required CT for disinfection. The ozone dose is adjusted to maintain an ozone residual in the effluent of Sections 2 and 3 that allows the required CT to be met.

A calculation of the actual CT being achieved is also programmed into to the SCADA system so it can be compared with the required CT equation. The actual CT in the ozonation chamber is calculated by multiplying the ozone residual and detention time in Sections 2 and 3. Section 1 is not included in the disinfection calculation because it was originally designed for taste and odor control. The following equation is used to calculate the actual CT; where C is the ozone residual (mg/L) in the effluent of Sections 2 and 3, V is the volume of the respective sections (gal), and Q is the water flow rate through the ozone chambers (gpm):

$$\text{Actual CT (mg/L}\cdot\text{min)}=0.7\left[C_2\left(\frac{V_2}{Q}\right)+C_3\left(\frac{V_3}{Q}\right)\right]$$

A baffling factor of 0.7 was determined by the MDH during the MWTP design. For the first six years the MWTP was in operation, the ozone residual was only measured for disinfection in Section 3 and target ozone residuals were developed based on water temperature and plant flows to maintain disinfection. The ozone residual or contact time in Section 2 were not taken into account for disinfection. After bromate formation became a concern in the early 2000s, ozone monitors were installed in Section 2 to measure the ozone residual and to earn additional disinfection credit. After the required CT and actual CT equations were programmed into the SCADA system, the MWTP began monitoring disinfection in real-time.

The CT ratio (actual CT/required CT) in each ozonation chamber is monitored to ensure disinfection compliance. If the CT ratio is greater than one, the disinfection process is within compliance. If the CT ratio is less than one, the disinfection process is out of compliance and operations must be altered to regain compliance. The most common cause for falling out of compliance is increased organics content in the water being ozonated. When the organics content increases, ozone that would otherwise be available for disinfection is used to oxidize the additional organics. Compliance may be regained by either increasing the ozone dose or decreasing the pH during recarbonation to increase the disinfection capacity of ozone. Ozone residual is reduced more rapidly as pH increases because ozone decay accelerates and the hydroxyl radical is more likely to form, as described in Section 2.2. By programming the required CT and actual CT equations into the SCADA system, the MWTP was able to simplify operation of the ozone system and maintain continuous disinfection compliance.

During the winter, when the Red River is frozen over and water being pumped into the plant is very cold, calcium thiosulfate is added to the ozone chamber effluent to ensure that no residual ozone is entering the filters. This is required due to the natural tendency of water to hold more air as the temperature decreases.

2.3.2.3. Filtration

The MWTP utilizes four dual media filters consisting of 24-inches of anthracite coal on top of 12-inches of filter sand. The media is supported by a 5-inch layer of torpedo sand above a false floor under drain system (Infilco-Degremont MONOFLOR®). The filters are fed by an influent channel containing weir boxes around each filter influent valve to ensure that each filter receives an equal portion of the total plant flow. Sodium hexametaphosphate ($(NaPO_3)_6$) is added in the filter influent channel for corrosion control in the distribution system. Sodium hexametaphosphate prevents corrosion by forming polyphosphate precipitation which forms a thin film on the pipe wall, preventing contact between water and the pipe wall. The filters were designed to have a maximum loading rate of 5.1 gallons per minute per square foot (gpm/ft^2). At a typical plant flow of 4.5 MGD the loading rate is 2.3 gpm/ft^2. Depending on influent water quality and filter performance, each filter operates for approximately 70 to 96 hours before being backwashed.

Filter backwash sequences are automated based on run time, but can also be controlled manually. Normal backwashes begin with an eight minute air scour to dislodge the media and break up any clumps or “mud balls” that may have formed. The media is then backwashed at a rate of 4,800 to 5,300 gpm, depending on the water temperature, until the media has been effectively cleaned, usually between 6 to 8 minutes. Backwash water is collected in backwash troughs before flowing into a washwater reclaim pit to be pumped back to the inlet structure of the plant. Based on the Filter Backwash Recycling Rule, recycled backwash water must be treated through the entire treatment process to reduce the risk of illness from *Cryptosporidium*. When the backwash is complete the media is allowed to settle; the lower specific gravity of anthracite allows it to settle on top of the sand media. Water is then filtered-to-waste for approximately one hour or until the filter’s effluent turbidity has dropped below 0.1 NTU. Under normal operating conditions the effluent turbidity of any individual filter is approximately 0.04 NTU.

The main purpose of filtration is turbidity removal to satisfy requirements set forth in the Surface Water Treatment Rule. However, they also have the added benefit of using biological filtration to remove by-products from the ozonation system. As stated previously, most organics are not completely reduced to carbon dioxide during ozonation but are broken down into more biodegradable forms. These biodegradable organics are consumed by microbes on the filter media, resulting in greater TOC reduction. Up to 20 percent TOC removal is achieved during the summer and fall, when biological activity is well established as a result of higher water temperatures. However, very little TOC removal is achieved in the winter when the water temperature is low. TOC removal in the MWTP filters from October 2013 to September 2014 is shown in Figure 17.

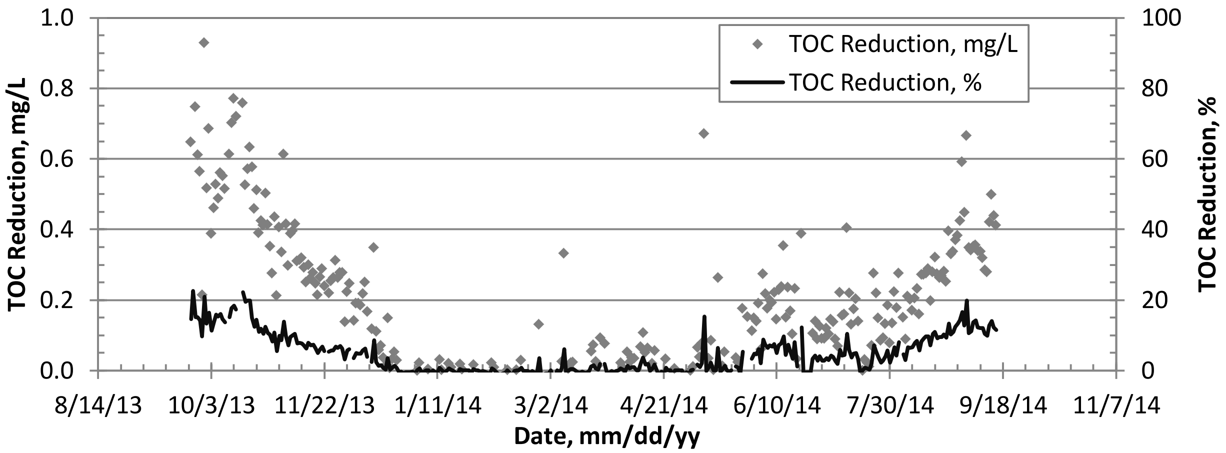


Figure 17: MWTP TOC removal during filtration (2013-2014)

2.3.2.4. Secondary Disinfection

After being filtered, water flows from the filter effluent channel into the clearwell, where it is chloraminated to provide secondary disinfection in the distribution system. Chloramination is achieved through the addition of chlorine and ammonia. Although three forms of chloramines exist (monochloramines, dichloramines, and trichloramines), MWTP employs monochloramines because they provide a stable disinfectant and have the least objectionable taste and odor. Monochloramines are also the type of chloramine that forms under conditions which are preferred for the water distribution system; the MWTP maintains a finished water pH between 9.10 and 9.30 to prevent corrosion in distribution piping and ensure that monochloramine is present. During the summer, when the pH in the ozone chamber must be depressed to help maintain the required CT for disinfection, soda ash is added in the clearwell to bring the pH back into the desired range. Finished water is pumped from the clearwell to underground storage reservoirs. The finished water is then pumped from the reservoirs by one of two high service pumping stations to the Moorhead's distribution system.

2.3.3. Bromate Formation Concerns and Changes to the Ozonation System

Bromate formation has been a concern at the MWTP since the plant was being designed because of the potential for bromate formation in the ozone disinfection system and because each water source contains bromide. Letters from the MWTP to the MDH from the early 2000s describe operational changes that had been made in the MWTP to prevent the formation above the bromate MCL. These changes include adding a carbon dioxide feed point to drop the pH in the ozone chamber earlier in the process and prevent ozonation at a high pH that could result in bromate formation, adding ozone monitors to Section 2 so that it could be used for CT calculations and less ozone could be dosed to meet disinfection requirements, adding a pre-ozonation ammonia feed point to use ammonia as a bromate inhibitor, and using pH depression as a method to decrease the ozone dose necessary for disinfection.

2.4. Previous Bromate Study at MWTP (2012)

A systematic bromate study was conducted at the MWTP in 2012 (Storlie, 2013). The study focused on quantifying bromate formation in the ozone disinfection process and identifying operational strategies to minimize bromate formation. Major findings and recommendations of the study are presented in the following subsections.

The specific objectives of the study included:

1) Determining bromide concentrations in the source waters;
2) Studying bromate formation in the ozonation process;
3) Evaluating the impact of operational parameters on bromate formation; and
4) Developing a mathematical model to simulate bromate formation under various operational conditions.

2.4.1. Source Water Bromide Concentration

Determining the bromide concentration in each of MWTP’s source waters was the first important step in determining the how bromate forms in the ozone disinfection process.

Before the 2012 study, the bromide concentration was only known for a few of Moorhead's water sources. In 2012, Red River bromide concentrations were analyzed at both the MWTP and the Fargo, North Dakota water treatment plant, and ranged from 24 to 109 ppb, with and average concentration of approximately 60 ppb. Groundwater samples from the Buffalo Aquifer (Wells 1, 2, 8, 9, and 10) contained between 50 and 84 ppb bromide, which is relatively low and close to the average Red River concentration. However, the Moorhead Aquifer (Wells 6 and 6B) contained 287 to 304 ppb bromide, or greater than four times the amount found, on average, in the Buffalo Aquifer. Results from source water samples analyzed for bromide in 2012 are shown in Figure 18.

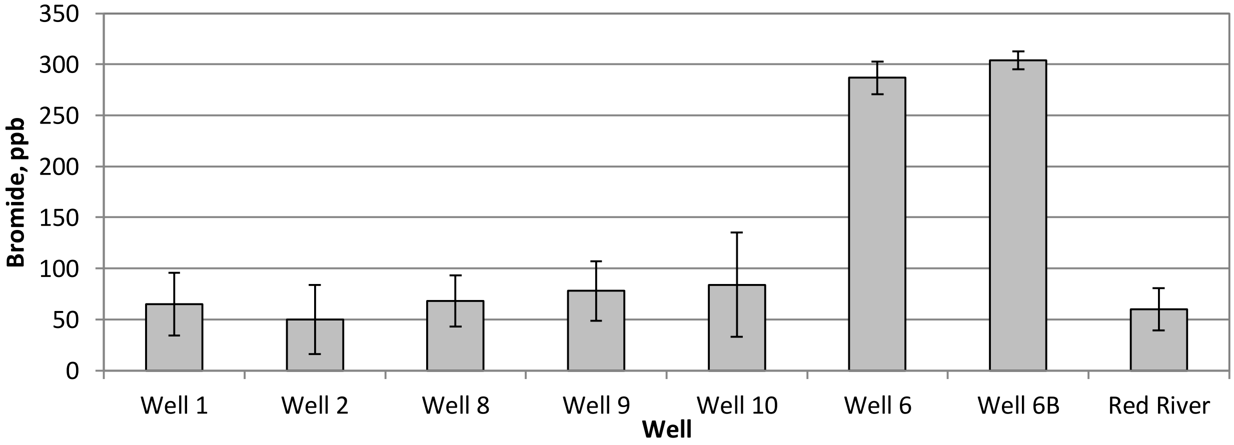


Figure 18: 2012 average source water bromide concentrations

2.4.2. Bromate Formation in the Ozone Disinfection Process

Bromate formation has been a concern of the MWTP since the ozone disinfection facility was put online in 1995. However, past bromate data was limited to results from monthly testing required by MDH that are used to determine MWTP's compliance with the bromate MCL. The 2012 bromate study provided the first opportunity to quantify bromate formation based on regular sampling.

Results from the 2012 sampling period suggested that bromate formation was a legitimate concern for the MWTP. For nearly two months at the beginning of summer 2012, bromate formed at concentrations greater than 10 ppb on a consistent basis and were often spiking to approximately 25 ppb (Figure 19). Nearly 40 percent of the ozone chamber effluent samples collected contained more than 10 ppb bromate. After samples for the two month period were analyzed, source water changes were made to limit the amount of bromate forming. Another bromate formation spike on August 3, 2012 helped determine that operational parameters can have a major impact on bromate formation.

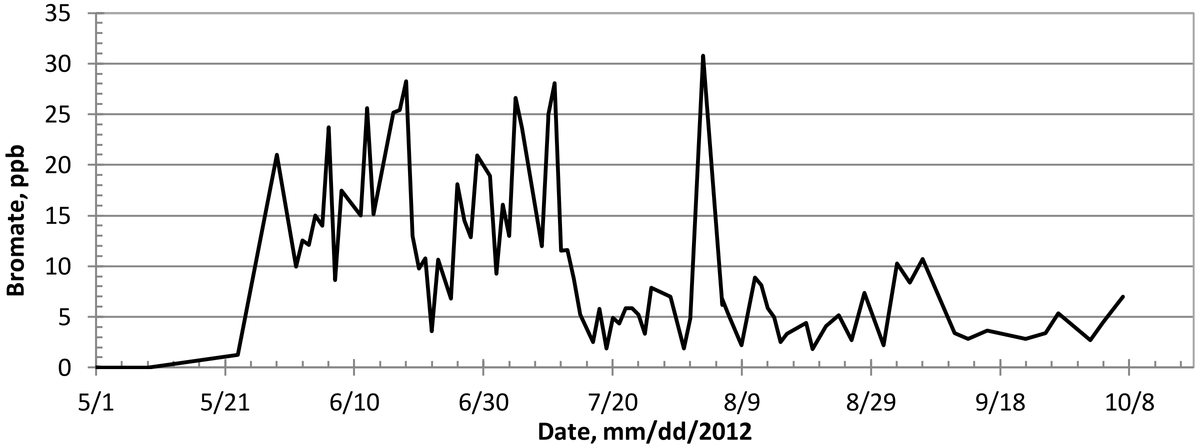


Figure 19: 2012 ozone chamber effluent bromate concentrations

2.4.3. Impact of Operational Parameters on Bromate Formation

After bromate formation in the ozone chamber was quantified, it was possible for Storlie to analyze the data and determine which operational parameters affect bromate formation most. In particular, Storlie was able to analyze bromate formation on August 3, 2012, when the bromate concentration in the ozone chamber spiked to 30.8 ppb. A heavy rain event on August 3 after a long period of dry weather caused drastic changes in the Red River water quality in regards to total hardness and organics content.

To combat the changing water quality in the Red River, the MWTP can either reduce the amount of river water being treated by using well water to supplement the flow or adjust the treatment process and attempt to treat the lower quality water. In the case of August 3, the MWTP was already treating both river and well water; after the unfavorable water quality was detected, the amount of river water being pumped into the plant was reduced and the percentage of well flow coming into the plant was increased. During this event wells 6B and 9 were being utilized. Well 6B is much softer than Moorhead's other groundwater sources so it was used to offset chemical costs of treating water with high hardness. However, as mentioned previously, Well 6B also has a very high bromide concentration when compared to MWTP's other sources and the source water change caused a spike in the MWTP influent bromide concentration.

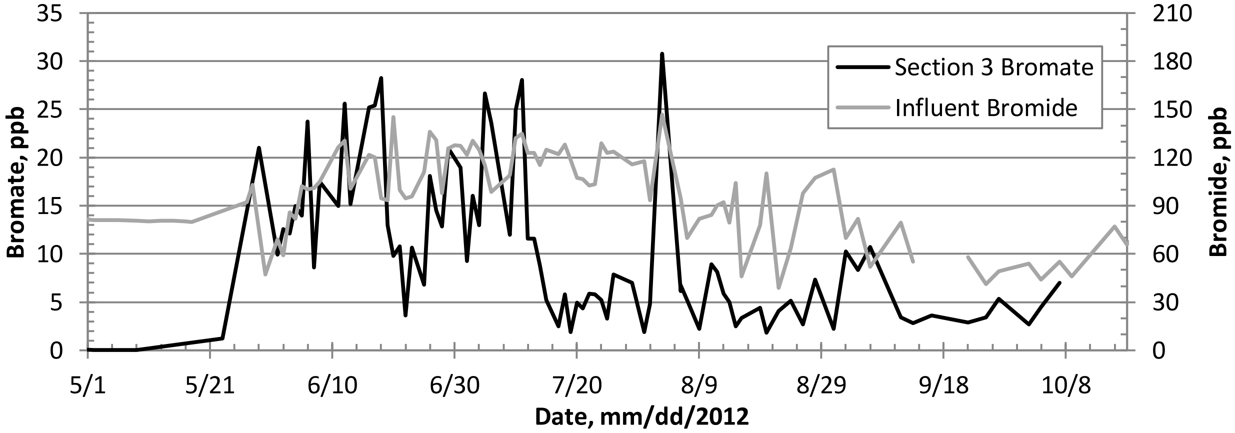


Figure 20: 2012 influent bromide concentration and bromate formation comparison

Bromate formation and the influent bromide in 2012 are compared in Figure 20. It can be seen that before the bromate spike occurred the influent bromide concentration was 94 ppb, and reducing the percentage of river water being treated caused the bromide concentration to increase to 147 ppb, an increase of approximately 156 percent.

Another operational factor that impacted the bromate spike was the ozone dose being applied to the water. To combat the increased Red River TOC, the ozone dose was increased to maintain disinfection compliance. However, the significant ozone dose increase, from 2.7 to 6.0 mg/L, provided excess ozone in the ozone chamber that was available to oxidize the additional influent bromide concentration. The correlation between the ozone dose increase and bromate spike is shown in Figure 21.

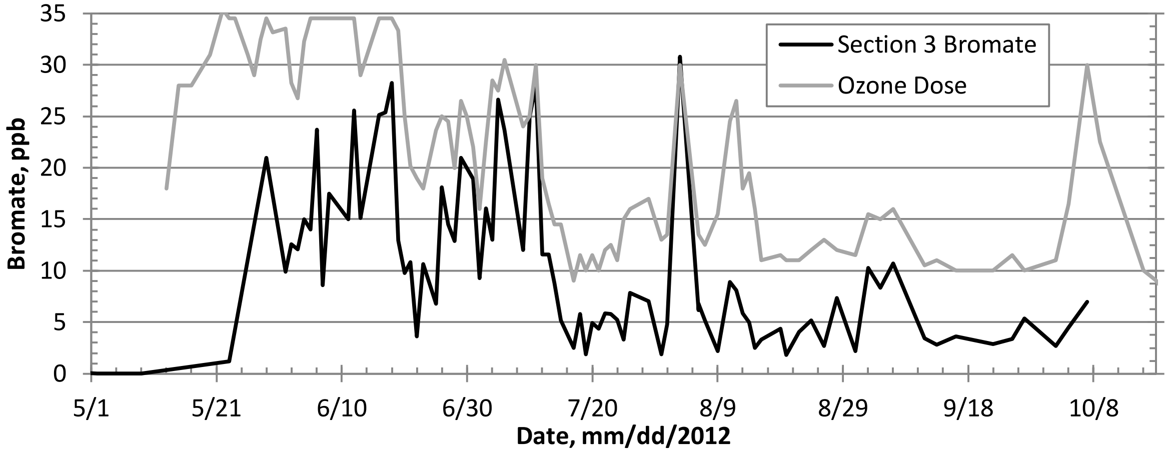


Figure 21: 2012 ozone dose and bromate formation comparison

Adding to the issues of increased bromide concentration and excessive ozone dose was increased water temperature. As mentioned previously, bromate formation is more of a concern in warmer water due to faster reaction rates that occur. In fact, Storlie concluded that bromate formation did not exceed 10 ppb when the water temperature was below 16.5°C. With that in mind, the water temperature rose from 16.8 to 19.8°C during the bromate spike on August 3, 2012 (Figure 22). The temperature rise of 3°C helped to increase reaction rates along the bromate formation pathways and was one of the causes for increased bromate formation.

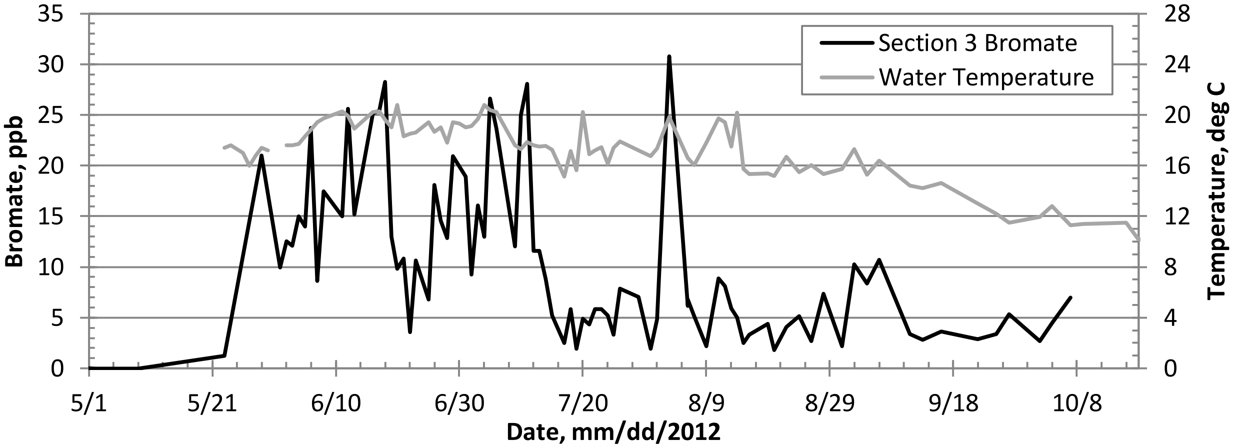


Figure 22: 2012 water temperature and bromate formation comparison

The bromate spike on August 3, 2012 helped give insight on how operational parameters at the MWTP can affect bromate formation. A combination of source water selection, increased bromide concentration, excess ozone dose, and increased water temperature laid the foundation for the bromate spike. Using knowledge of the August 3 event, operational strategies to reduce or mitigate the formation of bromate could be developed; these strategies are explained in more detail in Chapter 3.

2.4.4. Mathematical Bromate Formation Model

A significant portion of Storlie's research was developing a bromate prediction model based on sampling results. The prediction model, shown below, incorporated TOC, ozone dose, bromide, pH, and temperature and was able to represent day-to-day changes in bromate formation at the MWTP.

$$\text{BrO}_3^- = e^{-9.252} \times \text{TOC}^{-0.446} \times \text{O}_3\ \text{Dose}^{1.279} \times \text{Bromide}^{0.904} \times \text{pH}^{4.398} \times \text{Temperature}^{0.819}$$

The model found that ozone dose, bromide concentration, pH, and temperature have a positive correlation to bromate formation. Organics content (TOC) was found to be negatively correlated to bromate formation. These correlations were expected, and are backed by literature. Although the model was able to represent day-to-day changes, there was a high amount of variability between the modeled results and actual results. It would be beneficial for the MWTP to determine if the model is able to fit sampling results of this study and to reduce the variability in the model.

2.4.5. Findings and Recommendations of 2012 Study

After results from the 2012 bromate study at the MWTP were analyzed, Storlie made various recommendations based upon her conclusions and results. Some of the findings and recommendations of the 2012 study lead to operational changes that were implemented as part of this study because a major objective of this study was to determine if operational changes or process equipment improvements are effective in minimizing bromate formation. Results of this study will directly impact how the MWTP is operated in the future and will hopefully provide guidelines for future ozone process design.

Results from the 2012 study determined that, while the Moorhead Aquifer is the MWTP's softest source and may reduce chemical requirements for softening, it also has the highest bromide concentration available to be oxidized to bromate. It was also determined that high bromide concentrations, ozone doses, and water temperatures can lead to increased bromate formation during ozonation.

Various recommendations were also made as a result of the previous study. The first recommendation was to implement operational changes that could be used to minimize bromate formation. The ideal operational changes would not affect MWTP's overall treatment goals and would be easy to implement. It was also recommended to improve the bromate prediction model performance by collecting additional water samples to increase the amount of data used for developing the model.

2.4.6. Additional Work Required to Minimize Bromate Formation

A few water quality and operational parameters that were not considered with regard to bromate formation by the Storlie (2013) study were identified. These parameters include UV254, ammonia concentration, and the disinfection CT and CT ratio. The impact of UV254 needs to be studied to determine if aromatic carbons that absorb UV254 and may be broken down during ozonation have a greater impact on bromate formation than measurements of the total organics (i.e. TOC) in water. A relationship between the ammonia concentration in the water being ozonated and the amount of bromate that forms needs to be determined, as ammonia has been shown to reduce bromate formation (Section 2.2.6.). The impact of the disinfection CT and CT ratio should also be studied to determine if bromate formation increases with increasing CT ratios that would be caused by excess ozone in the water.

CHAPTER 3. METHODOLOGY

Methods used to achieve the objectives of this research are presented in this chapter. The sampling plan is explained in detail, as well as methods used to test for bromate and bromide. Methods and detection limits for other pertinent water quality parameters sampled are also presented in their respective sections.

3.1. Modifications to Ozone System and Operational Controls

This study differs from the previous study in a variety of ways due to operational changes that were developed and implemented for this study. The changes made include the installation of new ozone gas flow meters, discontinuing use of the Moorhead Aquifer during the summer, and reducing the target CT ratio achieved during disinfection. Additional water quality parameter impacts on bromate formation were also studied, including: UV254, DOC, hydraulic retention time, ammonia, sectional ozone dose, and CT ratio. The ammonia concentration in each of MWTP's water sources was also determined in this study, as not all of the sources had been previously quantified.

New ozone gas flow meters were installed at the MWTP between the 2012 and 2013 studies. These meters were an improvement over the old flow meters that required tapping on the flow meter housing in order to provide a reading. The new flow meters allow an exact fraction of the total gas flow to be added to each section and provided the first opportunity to accurately calculate the ozone dose being applied to each section. For example, the ozone feed valve to Cell A may be opened more than the feed valves to Cell C and Cell E so that more ozone is dosed in the first section of the ozone chamber to aid with taste and odor control. Prior to the installation of the new gas flow meters, the ozone being applied to each section was estimated by adjusting the manually-operated ball valves on the ozone feed gas piping. The gas flow meters will allow the impact of ozone dose on bromate formation to be studied on a section-by-section basis.

A major change implemented as part of this study was to discontinue using the Moorhead Aquifer as a source during the summer after it was determined that it contained four to five times more bromide than MWTP's other sources. The goal of this change was to decrease the concentration of influent bromide in the water that would be available to be oxidized to form bromate. It was expected that reducing the available bromide would effectively reduce bromate formation.

A past operational strategy at the MWTP was to dose ozone at a rate that maintained a CT ratio of 3.0 to 4.0 in an effort to reduce taste and odor compounds in the water. After the previous study determined that more bromate forms as the ozone dose increases the target CT ratio for this study was reduced to 2.0 in an attempt to reduce the amount of ozone applied to the water. It was expected that less excess ozone, that would otherwise be available to oxidize bromide, is added to the water by reducing the target CT ratio. This change does not affect MWTP's overall disinfection scheme because the USEPA-required CT will be continually met at a target CT ratio of 2.0.

3.2. Sampling Plan

The previous bromate study determined concerning levels of bromate formation only form during warm weather months, so the sampling plan for this study was determined based on the Storlie (2013) conclusion that bromate formation is more significant at temperatures above 16.5°C. Water samples were collected from May to November 2013 for analyses of bromate, bromide, pH, temperature, dissolved organic carbon, ultraviolet light absorbance, and ammonia. Sampling was conducted on a weekly basis when the water temperature was less than 15°C in case bromate greater than 10 ppb formed below the 16.5°C temperature proposed by Storlie. At temperatures greater than 15°C, samples were collected three times per week. Water temperature in the MWTP rose to 15°C in May and dropped below 15°C in October.

As part of the sampling plan, water quality parameters known to affect bromate formation were tested. Water quality parameters tested at each sample point are shown in Table 7. Cells marked with an "x" indicate the water quality parameter was tested from the point indicated in the column heading. Operational data collected from the MWTP at the time of sampling is explained in Section 3.3. Well samples were collected on a weekly basis, but only when water was being pumped from the respective well; the locations of MWTP's wells were described in Chapter 2. Red River samples were collected weekly for the duration of the study. The sample locations selected for each water quality parameter are explained below in their respective sections.

Table 7: Sampling locations

	Ozone chamber				Finished		
Test	Influent	Section 1	Section 2	Section 3	Water	Wells	Red River
pH	x	x	x	x	x		
Temp.	x	x	x	x	x		
DOC	x	x	x	x			
UV254	x	x	x	x			
Bromide	x			x		x	x
Bromate		x	x	x	x		
Ammonia	x			x		x	x

The finished water reservoir and Red River samples were collected from sample taps in the MWTP laboratory; the Red River sample is pumped from the Red River influent pipeline inside the MWTP. The sample location for the ozone chamber influent and Sections 1, 2, and 3 are shown in Figure 23. The ozone chamber influent sample was collected to analyze water before any ozone had been applied. At this point, the water has been softened, but no oxidation has been practiced. Samples were collected from the effluent of Section 1, Section 2, and Section 3 because after ozone is applied in the first cell of each section it is allowed to react in the second cell of the section before a sample is taken from the section's effluent. Also, by sampling after each ozonation point it should be possible to determine how each section impacts bromate formation.

When sampling the ozone chamber, samples were first collected from the ozone chamber influent; each of the water quality parameters was immediately tested or preserved to be tested at a later date. After all of the ozone chamber influent samples were either tested or preserved, Section 1 was sampled. After all of the Section 1 samples had been analyzed or preserved, the Section 2 samples were collected, and analyzed or preserved, before finally collecting the Section 3 samples to be analyzed or preserved. This strategy was selected because the time taken to analyze and preserve samples collected from each point is approximately equal to the hydraulic retention time in each section of the ozone chamber, which is about 9 to 12 minutes at summer water demands. This sampling strategy was selected in an attempt to collect samples from the same volume of water as it flowed through the ozone chamber, assuming plug flow conditions.

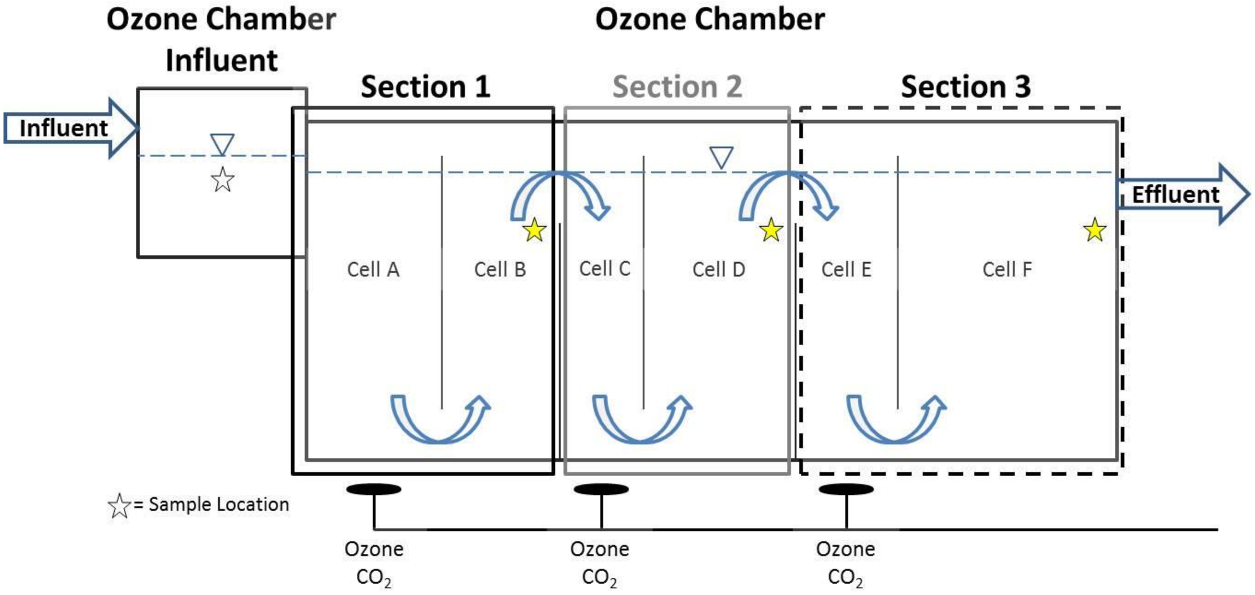


Figure 23: Ozone chamber sampling locations

3.3. Sample Analytical Methods

Water samples were collected from May to November 2013 for analyses of bromate, bromide, pH, temperature, dissolved organic carbon, ultraviolet light absorbance, and ammonia. The results from the analysis of each sample collected were investigated to determine each parameter's effect on bromate formation. Results of the sample analysis are presented in Chapter 4.

3.3.1. pH and Temperature

pH and temperature were measured using a Thermo Scientific Orion 815600 Ross combination electrode with an Orion 720A$^+$ meter, in accordance with Standard Method (SM) 4500-H$^+$ A (APHA, AWWA, WEF, 2005). Sample locations for pH were selected because pH is a determinant factor on bromate formation, as described in Chapter 2. By measuring pH throughout the ozonation process, it is possible to develop a correlation between pH and bromate formation. The pH meter was calibrated daily using a two-point calibration (pH 7.0 and pH 10.0) with pH 9.0 as quality control (Moorhead Public Service, 2011).

3.3.2. Organics content

As explained in Chapter 2, organics content is also known to impact bromate formation. Each sample taken from the ozone chamber influent and Sections 1, 2, and 3 were measured for dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nanometers (nm) (UV254). The purpose for determining UV254 in water samples, instead of just total organic carbon (TOC) or DOC, is that the oxidation of organics by ozone is most often incomplete, meaning the organics are not completely broken down to carbon dioxide. However, the organics' molecular structures are broken down, resulting in a drop in UV absorbance. This drop in absorbance is more measurable than the change in the concentration of TOC/DOC throughout the ozone chamber. DOC and UV254 were analyzed in accordance with USEPA Method 415.3: Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water (Potter & Wimsatt, 2003).

3.3.2.1. Dissolved Organic Carbon

Dissolved organic carbon was analyzed using an O-I Analytical Model 1010 TIC-TOC (Model 1010) analyzer from May to July 2013. MWTP purchased a new Aurora 1030W TOC analyzer (1030W) from O-I Analytical at the end of July 2013 because the Model 1010 analyzer broke. From July to November 2013, DOC samples were analyzed with the 1030W. DOC samples were filtered through 0.45-micron glass fiber filters and then preserved with sulfuric acid and stored at 4±2°C for less than the 28-day maximum holding period before being analyzed.

3.3.2.2. Ultraviolet Absorbance at 254 nm

UV254 was measured using a Hach DR/4000U spectrophotometer and one centimeter (cm) pass-through vials. A TOC standard with a concentration of 30 mg/L TOC, having an absorbance of 0.696 cm^{-1}, was used to calibrate the Hach DR/4000U prior to measuring UV254. The spectrophotometer wavelengths are checked semi-annually to ensure accuracy (Moorhead Public Service, 2011). UV254 is a nonspecific measurement so the minimum detection limit has not been determined with confidence (APHA, AWWA, WEF, 2005). A portion of the filtered DOC sample was used to analyze UV254 samples immediately after collection.

3.3.3. Ammonia

Ammonia nitrogen was analyzed in samples taken from the ozone chamber influent and Section 3 using a Thermo Scientific Orion 9512HPBNWP ammonia-sensing electrode, with an Orion 720A meter, in accordance with SM 4500-NH_3 D (APHA, AWWA, WEF, 2005). Proper membrane maintenance and calibration of the electrode was performed before each use. This method is able to measure ammonia ranging from 0.03-1,400 mg NH_3-N/L and is not affected by water color or turbidity. The ammonia probe was calibrated before each use using 0.02, 0.2, and 2.0 mg/L ammonia standards; a quality control standard of 0.04 mg/L was used to verify the calibration. The MWTP laboratory conducted a minimum detection limit (MDL) study on the ammonia probe and determined 0.02 mg/L to be the MDL. For this reason, the probe is calibrated between the 0.2 mg/L and 2.0 mg/L, as all water samples analyzed in the laboratory fall within this range. After collection, samples were preserved with sulfuric acid to a pH less than 2.0, and refrigerated at 4±2°C for less than the 28-day maximum holding period before being analyzed. These locations were selected for sampling to determine if ammonia entering the ozone chamber was converted by ozone or consumed by bromine intermediates to inhibit bromate formation. Ammonia samples were also collected from MWTP's water sources. Ammonia was also added to the ozone chamber influent during this study when the MWTP was treating 100 percent Red River water to increase the ammonia concentration of the water being ozonated. Ammonia was added with a target concentration of 0.20 mg/L NH_3-N; however, the pre-ozone ammonia feed system is not accurate, making it difficult to achieve a target concentration.

3.3.4. Bromide

Bromide samples were collected from the Red River and groundwater sources used during the sampling period to gain more information on raw water bromide concentrations. Red River samples were collected from a sample tap in the influent pipeline. Samples from MWTP's groundwater sources were collected at the wellhead, when the respective well was pumping, to ensure the sample was representative of only that well. However, Well 10 was not sampled, as it is mainly used as an emergency source of water and was not used during this study.

Samples from the ozone chamber influent and Section 3 effluent were also collected for bromide analysis. Ozone chamber influent samples were collected for the purpose of determining the bromide concentration entering the ozone chamber that was available to react with ozone. Ozone chamber effluent samples were collected to determine the amount of bromide remaining in the water after ozonation.

Bromide was measured using a Dionex ICS-3000 Ion Chromatograph at the MWTP. Samples were preserved and analyzed in accordance with USEPA Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography (Hautman & Munch, 1997). A Thermo Scientific Dionex IonPac^{TM} AS19 4x250 mm anion-exchange column was used for bromide analysis. Bromide samples did not require preservation other than storage at 2 to 5°C. A calibration curve was created before analyzing each batch of bromide samples to determine the minimum reporting limit (MRL).

Quality assurance/quality control (QA/QC) procedures were similar to that followed by Storlie (2013), which are detailed in USEPA Method 300.1 (Hautman & Munch, 1997) and Method 302.0 (Wagner et al., 2009). To ensure accuracy of each batch analysis, initial calibration checks, continuation calibration checks (CCCs), laboratory reagent blanks (LRBs), and laboratory fortified blanks (LFBs) were used. All calibration standards and fortifications solutions were prepared by the MWTP laboratory.

3.3.5. Bromate

Water samples were collected for bromate analysis from the effluent of Sections 1, 2, and 3 in the ozone chamber in an effort to determine how bromate formation progresses throughout the ozonation process. Bromate samples were also collected from MWTP's finished water reservoir to determine the concentration of bromate entering the distribution system. Bromate samples were not collected before ozonation because bromate is not typically found in natural waters. It was assumed no oxidation of bromide would take place in the treatment process before ozonation, and therefore bromate would not be present in the samples.

Bromate was also analyzed using a Dionex ICS-3000 Ion Chromatograph. Samples were preserved and analyzed in accordance with USEPA Method 302.0: Determination of Bromate in Drinking Water Using Two-Dimensional Ion Chromatography with Suppressed Conductivity Detection (Wagner et al., 2009). A Thermo Scientific Dionex IonPac^{TM} AS24

2x250 mm anion-exchange column was used as the second dimension column in Method 302.0. Bromate samples required preservation using ethylenediamine (EDA) and storage at 2 to 5°C for a maximum of 28 days. A calibration curve was created before analyzing each batch of bromate samples. The QA/QC for bromate analysis followed that provided in Method 302.0.

3.4. Operational Data Collection

For each sample, a variety of parameters were recorded from the MWTP SCADA system. The plant influent flow rate was recorded to calculate the detention time in the ozone chambers; when two chambers were operating the flow rate into each chamber was assumed to be equal because they were designed to be hydraulically equal. The ozone dose, ozone concentration, and total ozone generator gas flow entering the ozone chamber was recorded from the ozone generator control panel for each sample collected. The ozone gas flow and ozone residual in each individual section was also recorded from their respective instrumentation so the ozone dose and CT being applied to each section could be calculated. The required CT and actual CT were also recorded from the MWTP SCADA system when each sample was collected.

CHAPTER 4. RESULTS

Results of this study are presented in this chapter and compared to the results of Storlie (2013) study. Results from raw water sampling for bromide and ammonia, and bromate formation results from the ozone chamber are discussed in detail. Water quality characteristic results for temperature, bromide, pH, ammonia, ozone dose, organics content, and hydraulic retention time are also discussed, along with their relationship to bromate formation.

4.1. Source Water Bromide and Ammonia

Each of Moorhead's source waters, with the exception of Well 10 in the Buffalo Aquifer, was analyzed for bromide and ammonia during this study. Bromide results confirmed findings of Storlie (2013), but much of the ammonia data was unknown prior to this study. The raw water bromide data helped to confirm MWTP's new operational strategies regarding source water selection and the ammonia data provides important information due to ammonia's impact on bromate formation.

4.1.1. Red River Bromide and Ammonia Sampling Results

Red River bromide and ammonia samples were collected from the river intake pipeline on a weekly basis from May to November 2013. Bromide concentrations ranged from 27.0 to 76.3 ppb, as shown in Figure 24. The average bromide concentration during the sampling period was 53 ppb, and no definite seasonal trend was observed. The variance in bromide concentration is likely due to the Red River being surface water.

The ammonia nitrogen (NH_3-N) concentration in Red River samples ranged from below the detection limit of 0.02 to 0.07 mg/L (Figure 24). Ninety-two percent of the samples measured below 0.04 mg/L, and 36 percent of the samples were below the detection limit. The average NH_3-N concentration was 0.02 mg/L, including non-detect samples that were assigned 0.0 mg/L and are denoted as non-detect samples. Due to the low Red River NH_3-N concentration, and the knowledge that NH_3-N may prevent bromate formation (Chapter 2), the MWTP adds ammonia to the ozone chamber influent while treating 100 percent Red River water during the summer. In the past, the target NH_3-N concentration in the contact chamber influent has been 0.2 to 0.3 mg/L. However, the pre-ozonation ammonia dose has been controlled by a manually-operated ball valve and it is difficult to add an exact dose. Also, the target NH_3-N concentration was selected based on levels normally experienced in filter influent samples when wells were used as a supplemental source, but a target concentration that could be used for bromate inhibition was unknown.

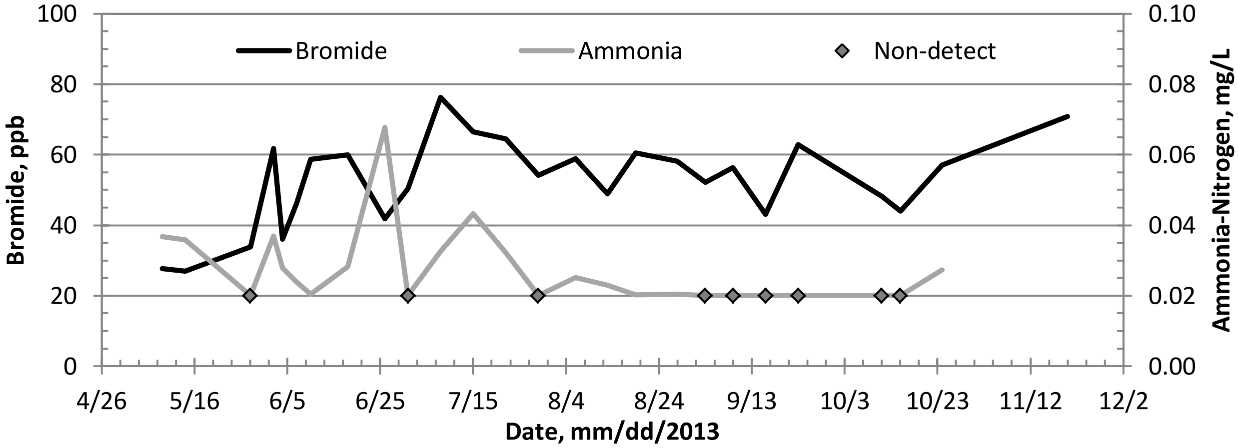


Figure 24: Red River bromide and ammonia-nitrogen concentrations

4.1.2. Groundwater Bromide and Ammonia Sampling Results

The MWTP has the ability to withdraw groundwater from seven wells in three different well fields; samples were collected and analyzed for bromide and ammonia weekly at each wellhead while water was being pumped to the MWTP. The results shown in Figure 25 are average bromide concentrations; the standard deviation (σ) is denoted by error bars for sources that had more than one sample analyzed. This study confirmed the Moorhead Aquifer contains more bromide than the Buffalo Aquifer. The Moorhead Aquifer wells (6 and 6B), have an average bromide concentration of 277 and 284 ppb, respectively, and an average concentration of 281 ppb in all of the aquifer samples collected. The Buffalo Aquifer (North and South) average bromide concentration ranged from 41 to 84 ppb. The average bromide concentration for all of the Buffalo Aquifer samples collected was 64 ppb. In comparison, the Red River has an average bromide concentration of 53 ppb. Based on averages, the Moorhead Aquifer contains approximately 4.4 times more bromide than the Buffalo Aquifer, and 5.3 times more bromide than the Red River. These results validate the decision to no longer use the Moorhead Aquifer during the summer when water temperatures make bromate formation a greater concern.

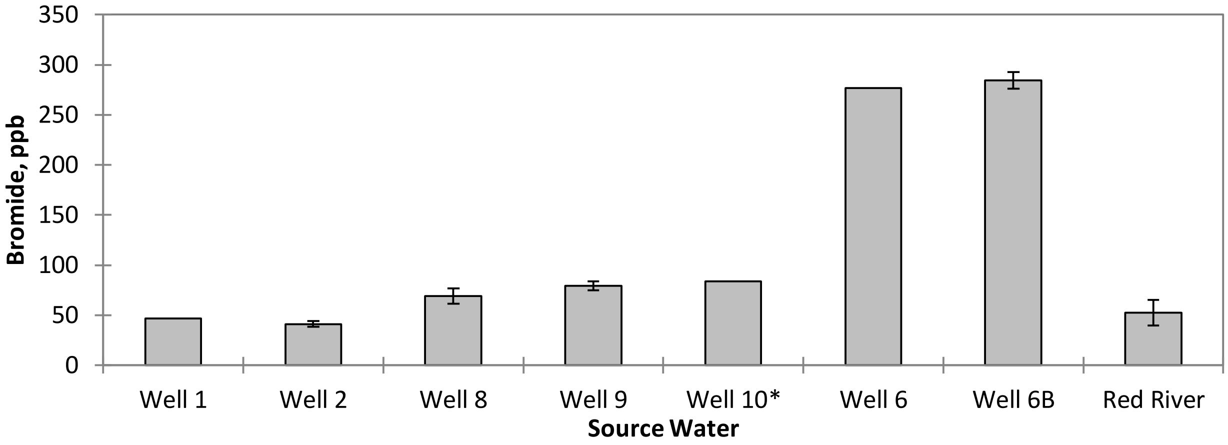


Figure 25: Source water bromide concentrations (*Well 10 sampled by MDH)

Ammonia nitrogen (NH_3-N) samples were collected simultaneously with bromide samples from each groundwater source. Before this study, the NH_3-N concentration in MWTP source water had only been analyzed in samples collected from the Red River and three wells (6, 9, and 10) by the MDH; however, it was generally known that the groundwater sources contained more NH_3-N than the Red River. Ammonia samples collected from the groundwater sources showed more variance when compared to bromide samples, as shown in Figure 26. The North Buffalo well field contained the lowest average NH_3-N concentration, with average concentrations of 0.37 and 0.31 mg/L for Well 1 and Well 2, respectively. The South Buffalo well field averages were 0.25 (Well 10, MDH analysis), 0.61 (Well 8), and 0.95 mg/L (Well 9). The Moorhead Aquifer wells contained the most ammonia, with average concentrations of 1.23 to 1.31 mg/L in Well 6 and Well 6B, respectively. In comparison to groundwater sources, the Red River has a very low NH_3-N concentration, averaging 0.02 mg/L. Error bars are used to indicate the standard deviation of ammonia analysis for sources that were analyzed more than once (Figure 26).

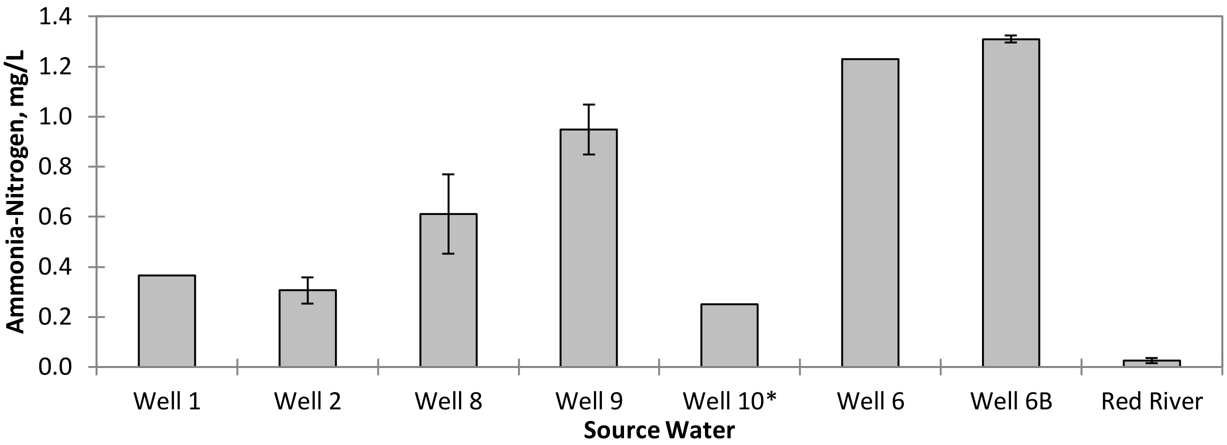


Figure 26: Source water ammonia concentrations (*Well 10 by MDH)

4.1.3. Ozone Chamber Bromide and Ammonia Concentrations

Bromide samples were also collected from the ozone chamber influent and Section 3 effluent; the results from these sampling points are shown in Figure 27. These locations were selected so the bromide concentration in the water could be verified. It was expected that the effluent bromide concentration would be slightly less than the influent, as the amount of bromide converted to bromate is low in comparison to the influent concentration. Bromide analysis results from the ozone chamber influent ranged from 24.2 to 121.1 ppb, with an average concentration of 60.7 ppb. The ozone chamber effluent (Section 3) analysis results ranged from 30.7 to 128.7 ppb, with an average concentration of 61.9 ppb. The average ozone chamber effluent concentration was 1.1 ppb (σ=8.9 ppb) greater than in the influent. There are a couple explanations for the ozone chamber effluent having an average concentration greater than the influent. The first is that bromate formation was very low and the small change in bromide concentration was not accurately reflected during analysis, which could be due to the method used. However, the average difference of 1.1 ppb is well within the recovery limits of the bromide analysis checks. A second explanation could be that small variations in bromide could have occurred between sample collection times from the influent and effluent of the ozone chamber.

When the Moorhead Aquifer was not used, the bromide concentration ranged between approximately 30 and 80 ppb. When the raw water temperature decreased to below 15°C after October 18, 2013, use of the Moorhead Aquifer was allowed. This caused the combined raw water bromide concentration to increase to approximately 120 ppb, an increase of more than 33 percent when compared to using the Buffalo Aquifer as the lone groundwater source.

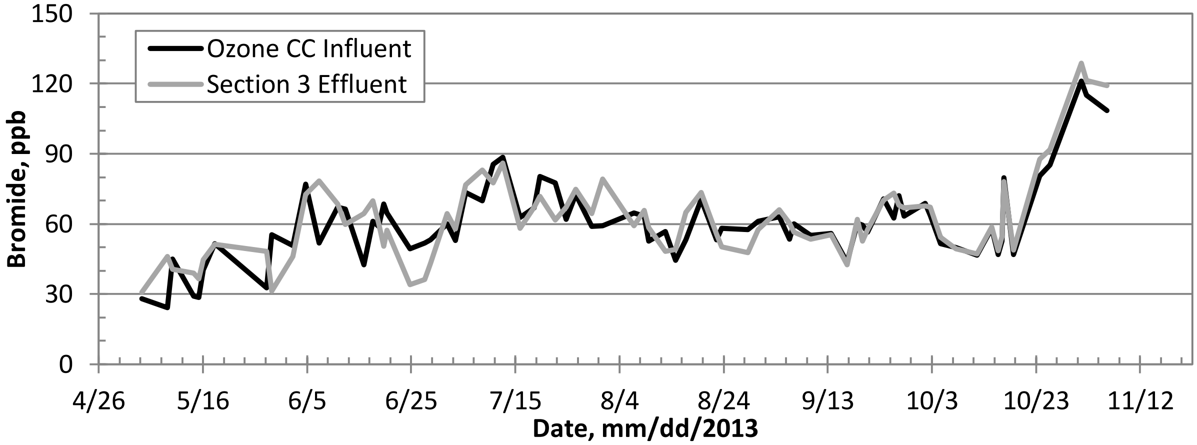


Figure 27: Contact chamber influent and effluent bromide concentration

Ammonia-nitrogen in the ozone chamber influent and Section 3 effluent was analyzed to determine if NH_3-N had an effect on bromate formation. It was suspected that if ammonia was reacting with hypobromous acid to form bromamines there would be a measureable drop in ammonia concentration between the sample points. Results from the sample analysis are shown in Figure 28. Ammonia concentrations in the ozone chamber influent ranged from 0.04 to 0.41 mg/L, and averaged 0.20 mg/L. The ozone chamber effluent results ranged from 0.05 to 0.40 mg/L, and also averaged 0.20 mg/L. The difference in analysis between the sample points ranged from 0.0 to 0.02 mg/L, with an average difference of nearly zero (3 percent) and standard deviation of 0.01 mg/L.

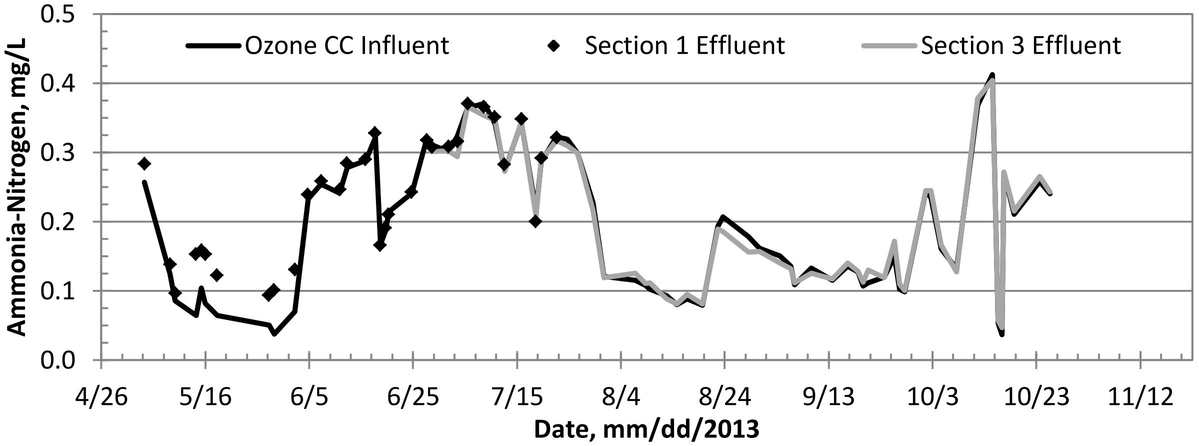


Figure 28: Contact chamber influent and effluent NH_3-N concentration

Ammonia was being dosed pre-ozonation from the beginning of the sampling period until June 18 – after this, well water increased the ammonia concentration until September 18, when the wells were turned off and ammonia was once again added pre-ozonation. The past strategy for dosing ammonia to the softening basin effluent was to open a manually-operated ball valve, making a target concentration very difficult to achieve. It should be noted that from May 10 to June 2 the ozone chamber influent sample was being taken directly from the softening basin effluent launders. During this period, the NH_3-N concentration in Section 1 was consistently higher than in the ozone chamber influent sample. It was suspected that the influent sample point might be too close to the ammonia feed point and that the sample was not well mixed. After June 2, the influent sample point was moved from the softening basin launders to the ozone chamber inlet to ensure samples were completely mixed. After it was determined that the ozone contact chamber influent and Section 1 influent provided the same result, the Section 1 effluent sample collection ceased.

Results from the ammonia analysis are not conclusive as to whether or not ammonia is consumed in amounts that would prevent bromate formation. A possible explanation for this is the concentration of ammonia is approximately ten to twenty times greater than the concentration of bromate in the ozone chamber, and the ammonia analysis method may not be sensitive enough to pick up the amount that reacts with free bromine species.

4.2. Effects of Operational Changes

Overall, operational changes made at the MWTP, including discontinuing use of the Moorhead Aquifer during the summer and lowering the CT ratio goal, were very effective in controlling bromate formation during this study. By discontinuing use of the Moorhead Aquifer during the summer the influent bromide concentration was reduced. By being cognizant of the ozone CT ratio, and knowing that excess ozone has the ability to form additional bromate, the MWTP reduced the amount of ozone applied to the water during disinfection. These changes allowed the average bromate formation occurring in the ozone chamber to be cut by more than half. The results of this study show that the MWTP was able to successfully reduce bromate formation in a full-scale disinfection facility through operational changes that did not change the overall treatment goals of the plant.

4.2.1. Discontinuing Moorhead Aquifer Use During Summer

The most impactful change resulting in decreased bromate formation is likely the reduction in influent bromide. In 2012, the influent bromide concentration ranged from 38 to 147 ppb, with an average concentration of 94 ppb. In 2013, the range was reduced to 24 to 89 ppb (average=61 ppb) when the Moorhead Aquifer was not used. The average reduction in influent bromide between 2012 and 2013 was 33 ppb, or 35.3 percent, as shown in Figure 29. The influent bromide reduction is entirely due to discontinued use of the Moorhead Aquifer. It is expected that this operational change was effective because less bromide was available in the water to be oxidized and form bromate. By recalling that literature has found approximately 17 percent of influent bromide is converted to bromate during ozonation (Song et al., 1997), it can be expected that bromate formation would decrease as a result of lowering the influent bromide concentration. The concentration of free bromine available to be oxidized by ozone would correspondingly be reduced as a result of decreasing the influent bromide.

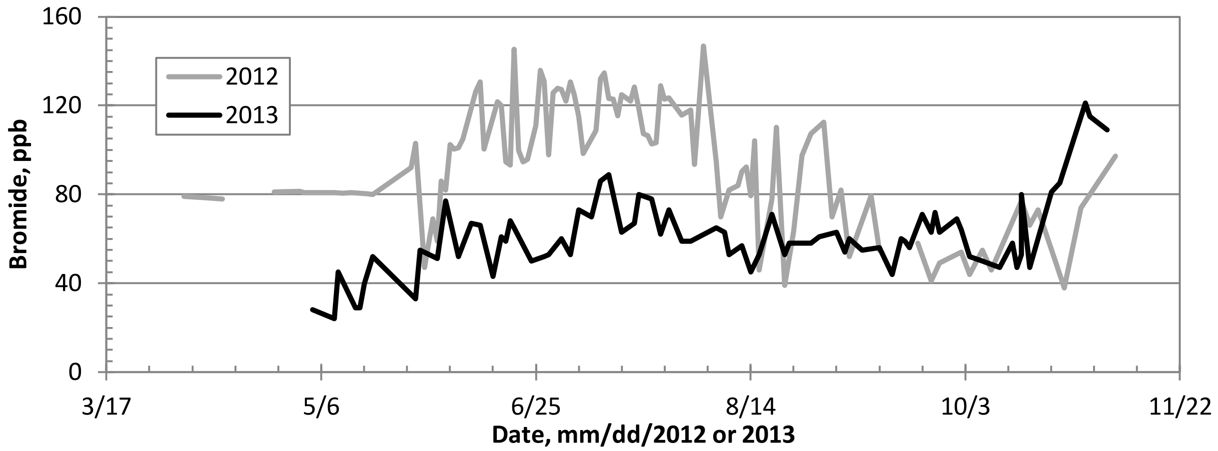


Figure 29: 2012 and 2013 influent bromide concentration comparison

4.2.2. Reducing Target CT Ratio

Another operational change implemented during this study was reducing the target CT ratio. In the past, when there was not as much concern that over-ozonating would increase bromate formation, the MWTP ozone system was often operated at a CT ratio of 3.0 to 4.0 in an effort to provide more taste and odor control. This strategy results in adding excess ozone to the water. After Storlie (2013) determined bromate formation is a major concern, the target CT ratio was reduced and the MWTP has not noticed an increase in taste and odor complaints, which may indicate that the excess ozone applied in the past did not have the desired effect.

Table 8: Comparison of 2012 and 2013 CT ratios

Parameter	2012	2013
Average CT ratio	2.62	2.18
Maximum CT ratio	9.68	3.95
Minimum CT ratio	1.25	1.09
Sample size	100	69
Samples > 2	75	39
Percent > 2	75%	57%

The average CT ratio for all samples taken was reduced from 2.62 in 2012 to 2.18 in 2013 (Table 8). The percentage of samples having a CT ratio greater than 2.0 was also reduced from 75 percent in 2012 to 57 percent in 2013. The reason for more than half of the samples having a CT ratio greater than 2.0 is that it is very difficult to maintain a ratio less than 2.0 when the required CT is very low. For example, if the required CT is 0.25 mgL^{-1}min at 20°C, it is much more difficult to keep the actual CT below 0.50 mgL^{-1}min than it is to keep it below 1.0 mgL^{-1}min when the required CT is 0.50 mgL^{-1}min at 10°C. The difference in 10°C allows two times more CT to be applied to the water while still maintaining a CT ratio below 2.0. Oftentimes, when the water temperature is warm and a low CT is required, the MWTP SCADA will alarm when the CT ratio is below 2.0 because of the ozone monitor sensitivity and the tendency for the ozone residual to bounce around, causing a quick drop in the CT being calculated. The CT ratio between 2012 and 2013 is compared in Figure 30.

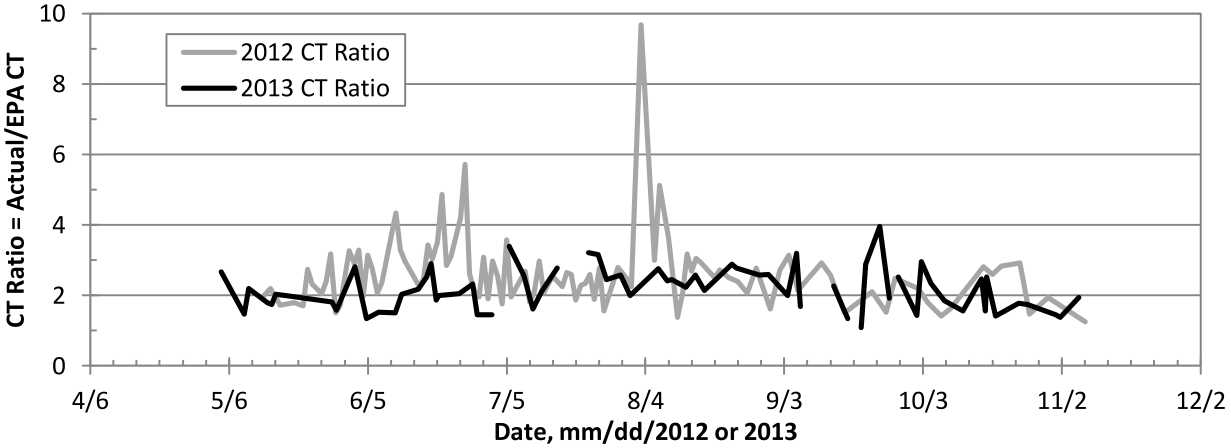


Figure 30: 2012 and 2013 ozone CT ratio comparison

4.3. Bromate Formation in the Ozone Chamber

The bromate concentration in the ozone chamber was measured at the effluent of Sections 1, 2, and 3 to determine how bromate formation progresses during ozonation. Bromate samples were also collected from the finished water reservoir to determine the concentration entering the distribution system. Each ozone chamber section is made of two cells; ozone is applied in the first cell and the sample point is located at the effluent of the second cell so ozone has had time to react and potentially form bromate.

4.3.1. Total Bromate Formation

During this study, 75 samples were analyzed for bromate formation from each sample point in the ozone chamber. Only seven of these samples (9.3 percent) contained more than 10 ppb bromate. Cumulative bromate formation in the ozone chamber ranged from zero to 17.9 ppb, with an average concentration of 4.5 ppb (Figure 31). Very little bromate formed in the month between June 25 and July 25, 2013. A possible explanation for this is that the hydraulic residence time (HRT) for that period was lower than for the rest of the study because only one ozone contact chamber was being used to treat a flow of 5 MGD or higher. The decreased HRT reduced the time ozone was able to react with the water. The impact of HRT on bromate formation is discussed in more detail in Section 4.4.7. It should be noted that the concentration of bromate in water is very low (parts per billion) and any error in the sample procedure could impact the analysis. For this reason, a small number of samples containing greater than 10 ppb bromate may not be as concerning as it appears.

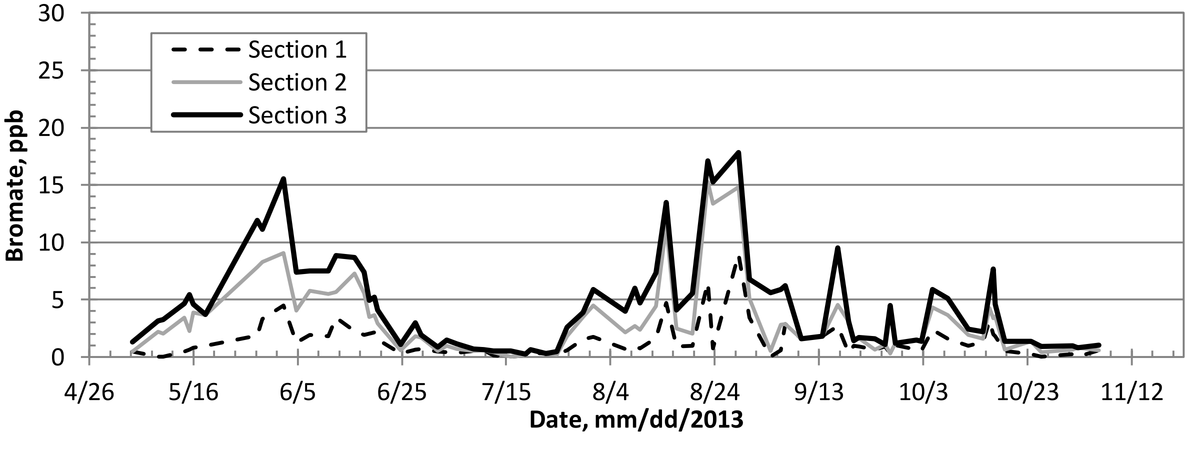


Figure 31: Cumulative bromate formation during ozonation

In order to determine the actual concentration of bromate entering the distribution system, the 2013 sampling plan included the effluent of the finished water reservoirs; the results from these samples are shown in Figure 32. Only two of these samples (2.7 percent) contained greater than 10 ppb bromate. Analysis results ranged from zero to 11.2 ppb bromate, with an average concentration of 3.2 ppb. It is important to note that samples collected from the ozone chamber are grab samples and may not be representative of bromate formation over an extended period of time. Reservoir samples are able to show the concentration of bromate formed during ozonation over a longer period. Also, the MWTP was never out of compliance with the bromate MCL over the course of this study, as the MCL is calculated based on a running annual average.

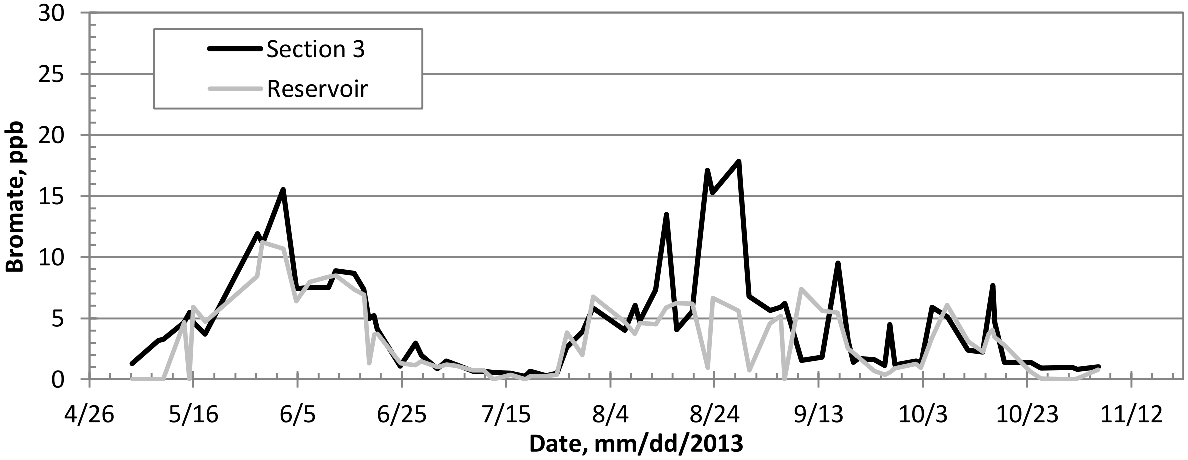


Figure 32: Comparison of contact chamber and reservoir bromate concentrations

4.3.2. Sectional Bromate Formation

The sectional bromate formation, or the bromate formed in an individual section, was determined by subtracting the bromate concentration of the preceding section from the concentration of the section being studied. For example, to determine the sectional formation in Section 2 the bromate concentration of Section 1 must be subtracted from the concentration in Section 2. Sectional bromate concentrations in the ozone contact chamber throughout the 2013 sampling period are shown in Table 9 and Figure 33. Results from this study confirmed the findings of Storlie (2013) and determined that the average bromate formation in Section 1 is less than in Sections 2 and 3.

Table 9: Sectional bromate formation in 2013

Bromate Formed	Units	Section 1	Section 2	Section 3
Minimum	ppb	0.0	0.0	0.0
Maximum	ppb	8.9	12.6	6.5
Average	ppb	1.35	1.78	1.43
Percent of Total	%	29.66	39.07	31.27

Further analysis of water quality parameters on a sectional basis is required to develop conclusions regarding the sectional bromate formation. Storlie (2013) observed that pH impacted bromate formation in Sections 2 and 3 more than in Section 1 and that Section 1 reduces more organics than Sections 2 and 3. However, it was not possible to measure the ozone gas flow to each section during the previous study because the new flow meters were installed as part of this study. The impact of sectional ozone dose on bromate formation is discussed below.

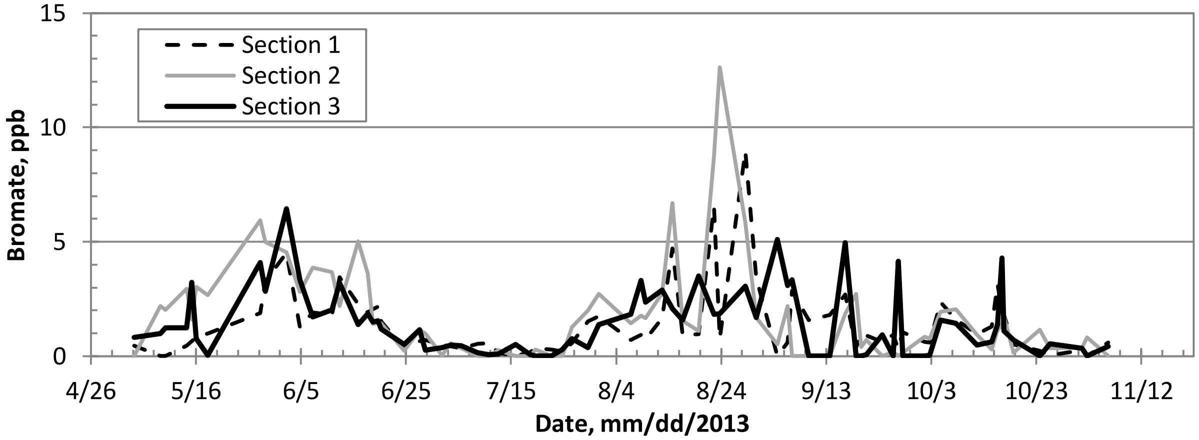


Figure 33: Sectional bromate formation in the MWTP contact chamber

4.3.3. 2012 and 2013 Bromate Formation Comparison

The most effective way to determine the success of the operational changes made during this study is to compare bromate formation between 2012 and 2013. A comparison of the bromate formation between the two studies is shown in Table 10. These results show that the operational changes made significantly reduced bromate formation in the MWTP. In 2012, 38.9 percent of the samples collected contained more than 10 ppb bromate, compared to only 9.3 percent in 2013. Also, the average bromate concentration was reduced from 9.7 to 4.5 ppb and the maximum bromate concentration was reduced from 30.8 to 17.9 ppb.

Table 10: Comparison of 2012 and 2013 bromate formation

	Parameter	Units	2012	2013
	Sample Population	#	90	75
Section 3	Samples over 10 ppb	#	35	7
		%	38.9	9.3
	Average BrO3 Concentration	ppb	9.7	4.5
	Maximum BrO3 Concentration	ppb	30.8	17.9
Reservoir	Samples over 10 ppb	#	-	2
		%	-	2.7
	Average BrO3 Concentration	ppb	-	3.2
	Maximum BrO3 Concentration	ppb	-	11.2

The effectiveness of the operational changes made is shown in Figure 34, which illustrates the drastic reduction in bromate formation between the two studies. It can be seen that the reservoir effluent, which is the water being pumped into the distribution system, contained even less bromate than the ozone chamber effluent in 2013. This suggests that samples collected from the baffled reservoirs may represent bromate formation over a longer period of time when compared to grab samples collected from the ozone chamber.

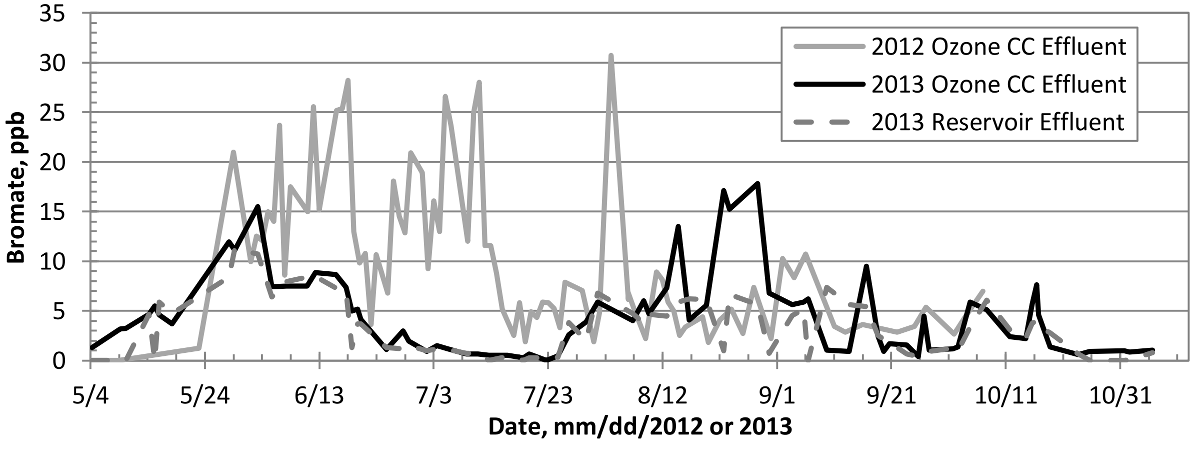


Figure 34: 2012 and 2013 total bromate formation comparison

4.4. Factors Impacting Bromate Formation

As described in Chapter 2, water temperature, bromide concentration, pH, ammonia, ozone dose, and organics concentration all affect the amount of bromate that forms in an ozone disinfection process. The relationships between these water quality parameters and bromate formation during this study are described in this section. Operational parameters, including CT ratio and hydraulic retention time, are also described in this section.

4.4.1. Impact of Temperature on Bromate Formation

Literature has shown that bromate formation is positively correlated to water temperature, as described in Chapter 2. The previous study approximated that 16.5°C was the breakpoint temperature with respect to bromate formation greater than 10 ppb in the MWTP. Additionally, all samples containing more than 10 ppb bromate during this study were collected when the water temperature was greater than or equal to 16.4°C. A general trend showing that bromate formation increases at higher temperatures, which is consistent with the literature (Galey et al., 2001; Siddiqui & Amy, 1993; Legube et al., 2004; Storlie, 2013), can be seen in Figure 35. However, some samples having a temperature greater than 20°C contained very little bromate indicating that, while temperature does impact bromate formation, it is not the only impactful parameter under all treatment conditions. Since more than 10 ppb bromate did not form at temperatures below 16.4°C in two consecutive studies, MWTP is only concerned with formation at higher temperatures and is comfortable with operations at lower temperatures. A critical temperature of 15°C was set to provide a buffer, as there is not enough evidence to determine 16.4°C is the lowest temperature that bromate will form over 10 ppb. Also, Galey et al. (2001) determined 15°C to be a critical temperature with regard to bromate formation. Bromate formation is increased at higher water temperatures because reaction rates are increased and because free bromine equilibrium shifts towards BrO^- being the dominant species at lower pH values.

The shift in equilibrium increases the concentration of free bromine that is able to react with ozone (Legube et al., 2004; Arvai et al., 2012).

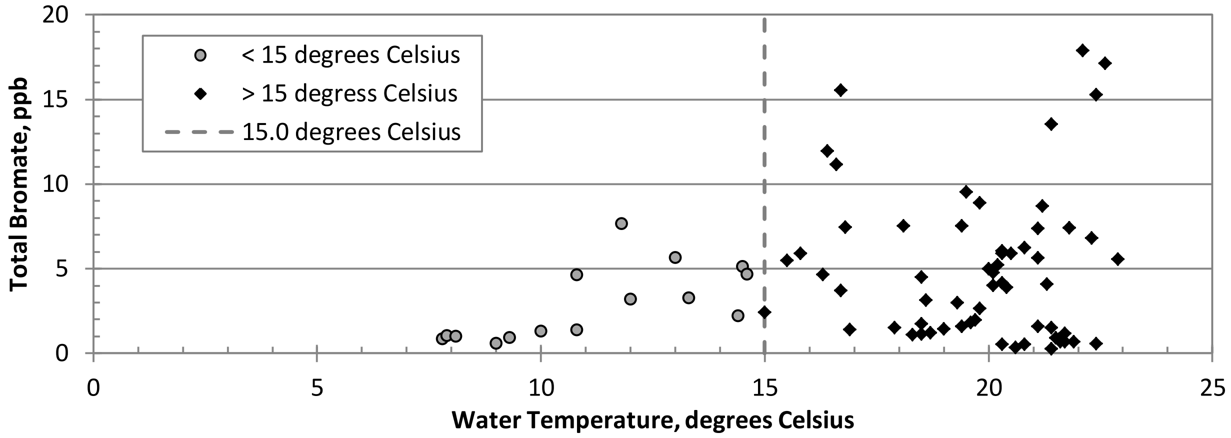


Figure 35: Bromate formation versus water temperature

4.4.2. Impact of Bromide on Bromate Formation

The bromide concentration in the ozone contact chamber influent was used to evaluate bromide's impact on bromate formation. The contact chamber influent bromide concentrations during this study ranged from 29 to 89 ppb. No apparent trend can be determined from the data (Figure 36), as all of the samples containing bromate greater than 10 ppb had a low to mid-range bromide concentration, ranging from 33 to 58 ppb. A reason for this is that the bromide concentration in the water being treated had a very small range; approximately 71% of the influent samples contained 50 to 70 ppb bromide. The relatively constant bromide concentration makes it difficult to draw conclusions based on this data. Although bromide concentration may not provide conclusive results to the impact on bromate formation, the concentration of free bromine (BrO^-) available to be oxidized by ozone is impacted by pH, and may impact the correlation. This impact is described in the following subsection. Modeling the data will allow a relationship between bromide concentration, bromate formation, and other water quality parameters to be determined.

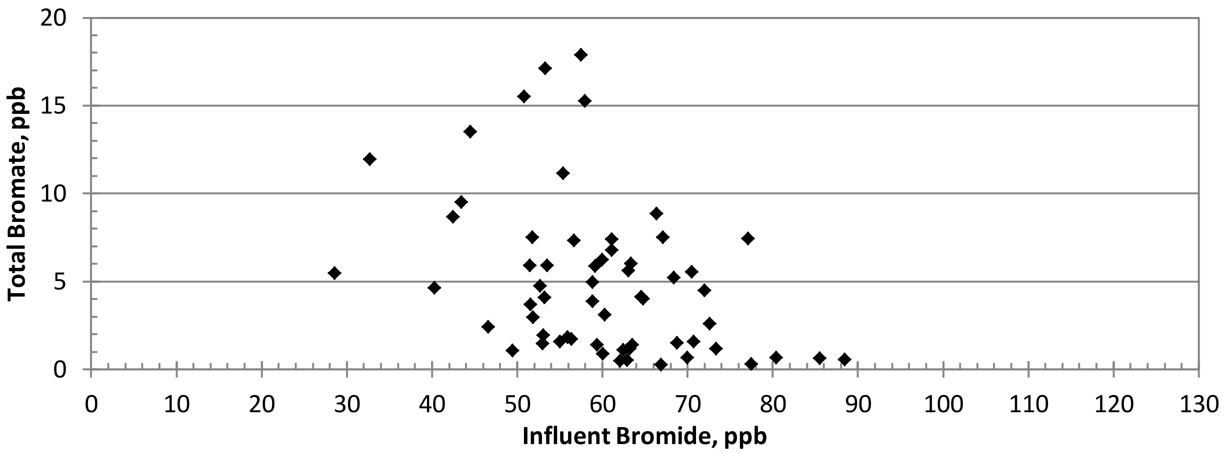


Figure 36: Bromate formation versus influent bromide concentration

4.4.3. Impact of pH on Bromate Formation

Samples from the ozone contact chamber influent and the effluent of each section were analyzed for pH. According to the Storlie (2013) bromate prediction model, pH was the most impactful parameter with regard to bromate formation. The MWTP ozonated at a high pH in Section 1 by feeding carbon dioxide (CO_2) in Section 2 when the water temperature was less than 15°C and then switched the CO_2 feed point to Section 1 when the water temperature increased. The pH range for each section, along with the average percentage of bromate formation in each section, is provided in Table 11.

Table 11: Sectional pH ranges in relation to bromate formation

	Units	Section 1	Section 2	Section 3
Minimum	pH	8.75	8.67	8.48
Maximum	pH	9.90	9.73	9.72
Bromate Formation (avg.)	%	29.66	39.07	31.27

The impact of sectional pH on bromate formation from when the temperature was greater than 15°C is shown in Figure 37, Figure 38, and Figure 39. There is a general trend showing that bromate formation increases with increasing pH in all three sections of the ozone chamber, which is consistent with the literature (Williams et al., 2003; Song et al., 1997;

Westerhoff et al., 1998). If Figure 2 is recalled, the percentage of BrO^- present in $HOBr/BrO^-$ equilibrium increases from approximately 45 to 90 percent as the pH increases from 8.70 to 9.70, which was the approximate ozonation pH range during this study. Bromate formation is increases as a result because BrO^- is the reactive species with molecular ozone. Also, the hydroxyl radical forms more rapidly as pH increases; it also reacts with BrO^- approximately two times faster than it does with HOBr (Legube et al., 2004). The combined effect of additional hydroxyl radical and BrO^- present in the water is that bromate formation increases.

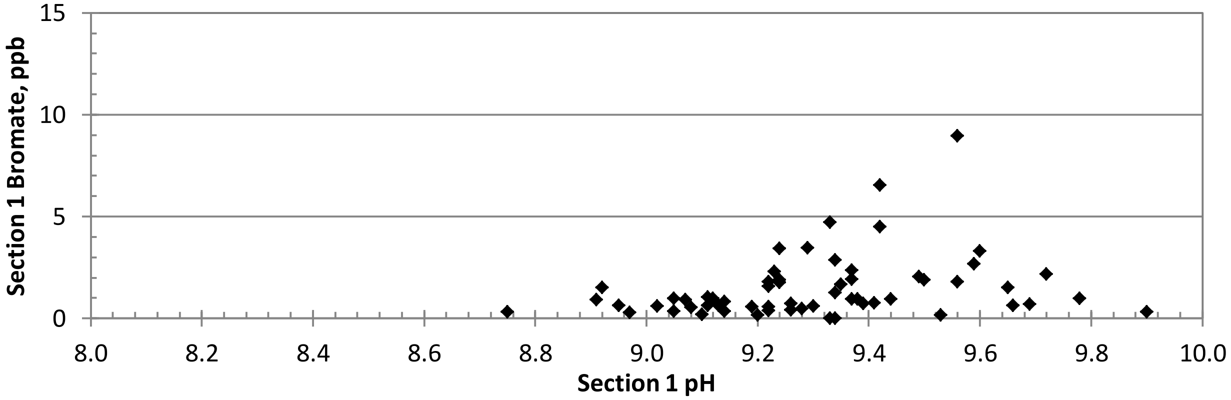


Figure 37: Section 1 bromate formation versus pH

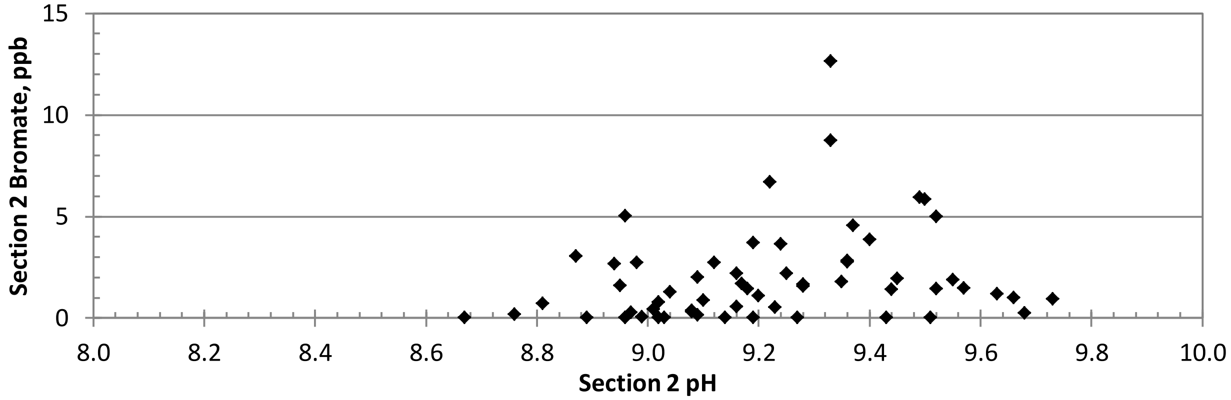


Figure 38: Section 2 bromate formation versus pH

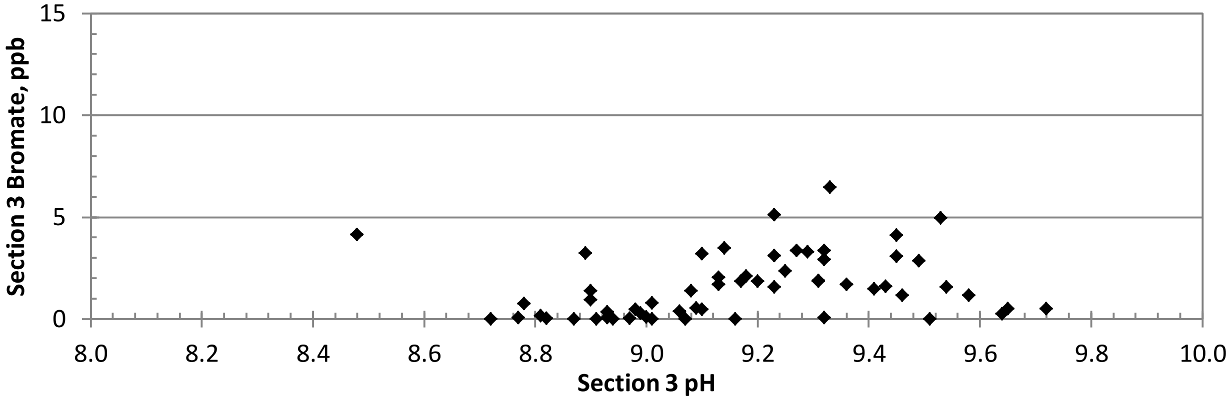


Figure 39: Section 3 bromate formation versus pH

4.4.4. Impact of Ammonia on Bromate Formation

Ammonia nitrogen samples were collected in the ozone contact chamber influent and effluent to determine the impact of NH_3-N on bromate inhibition and to determine if the concentration changes during ozonation. The NH_3-N concentration in the ozone chamber influent ranged from 0.08 to 0.37 mg/L when the water temperature was greater than 15°C, with an average concentration of 0.20 mg/L. Bromate did not form over 10 ppb when the NH_3-N concentration was greater than 0.21 mg/L, although 7 to 9 ppb bromate formed at NH_3-N concentrations up to 0.32 mg/L. There is a weak trend in Figure 40 showing decreased bromate formation as the ammonia concentration is increased. The lack of conclusive results with regard to bromate inhibition may be due to the ozonation pH. If Figure 3 is recalled, the optimum pH for bromamine formation is approximately 9.0, which is near the lowest ozonation pH during this study. As the pH increases from 9.0 to 9.7, bromamines do not form as readily because the HOBr available to react with NH_3 is reduced from approximately 50 to 10 percent of the free bromine species.

A preliminary goal for the MWTP should be to set a NH_3-N target of 0.30 mg/L in the ozone chamber influent, as the highest concentration of bromate to form above this level was 7.38 ppb. Also, literature has determined that as little as 0.5 mg/L ammonia can reduce bromate formation by approximately 75 to 80 percent (Neemann et al., 2004). After a precise pre-ozonation ammonia feed system is installed, the NH_3 impact on bromate inhibition could potentially be more easily determined and MWTP could change the target.

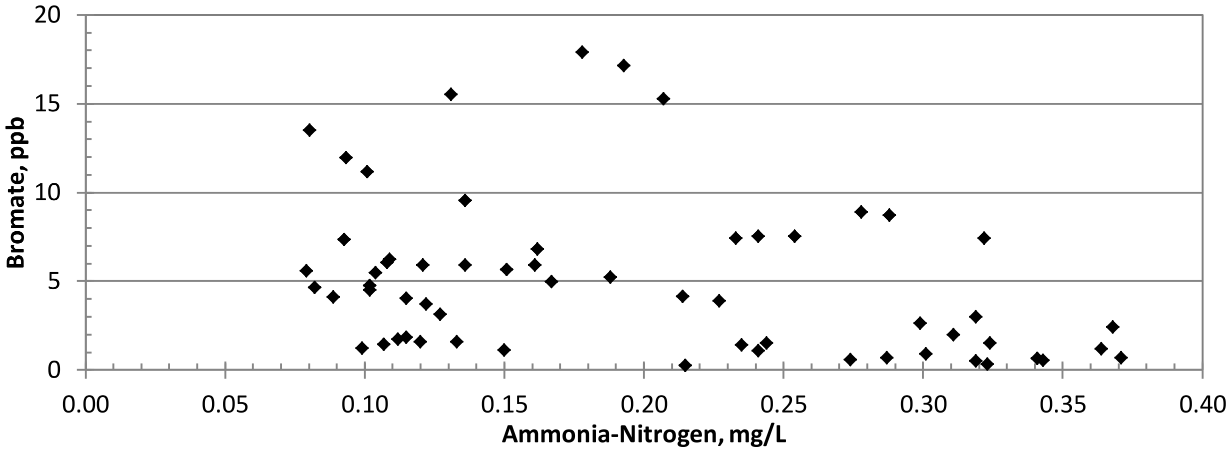


Figure 40: Bromate formation versus contact chamber influent ammonia

4.4.5. Impact of Ozone Dose on Bromate Formation

The ozone dose applied to water for disinfection has an impact on the amount of bromate formation that occurs. For the purposes of this study, the impact of ozone on bromate formation was studied in terms of total ozone dose, sectional ozone dose based on ozone gas flow to each section, and the ozone CT ratio. The results of this analysis are presented below.

4.4.5.1. Impact of Total Ozone Dose on Bromate Formation

The total ozone dose ranged from 2.9 to 8.0 mg/L throughout this study. As an in-house rule, the maximum dose MWTP will apply to water is 8.0 mg/L. Results from this study determined that bromate formation generally has a positive correlation to total ozone dose (Figure 41), which agrees with the literature (Galey et al., 2001; Guo et al., 2007; Song et al., 1997; Storlie, 2013). However, four of the seven samples containing more than 10 ppb bromate occurred at relatively low ozone doses of 5.0 to 6.2 mg/L, suggesting that other water quality parameters impacted the bromate formation in those samples.

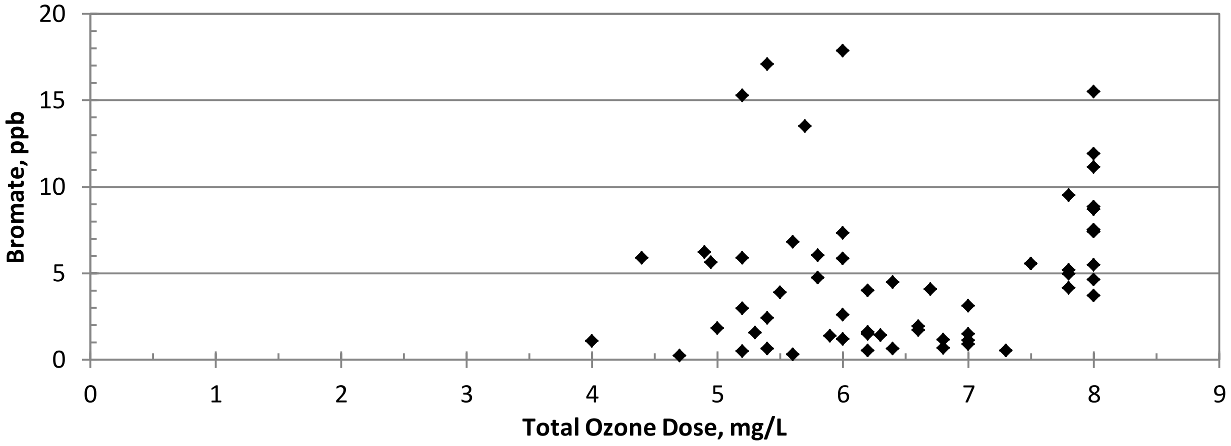


Figure 41: Bromate formation versus total ozone dose

4.4.5.2. Impact of Sectional Ozone Dose on Bromate Formation

The sectional ozone dose, or the dose being applied to an individual section, was determined based on gas phase ozone concentration and ozone gas flow rate to each section. The ozone concentration and gas flow to each section was recorded when samples were collected from the respective sections. A typical pressure swing adsorption system air density of 1.4403 g/L was used to convert the calculated ozone dose from liters of ozone per liter of water (L O_3/L H_2O) to milligrams of ozone per liter of water (mg O_3/L H_2O) (Rakness, 2005).

The total calculated ozone dose based upon gas flow data collected ranged from 2.9 to 8.2 mg/L. The total ozone dose set (set dose) at the ozone generator control panel versus the calculated total ozone dose (calculated dose) based upon gas flow data recorded is shown in Figure 42 – the dashed line represents a perfect correlation between the set dose and calculated dose. The difference between these two doses ranged from the calculated dose being 1.4 mg/L less than to 0.3 mg/L greater than the set dose. On average, the calculated dose was 0.3 mg/L (4.1 percent) less than the set dose. The standard deviation between the two values was 0.3 mg/L.

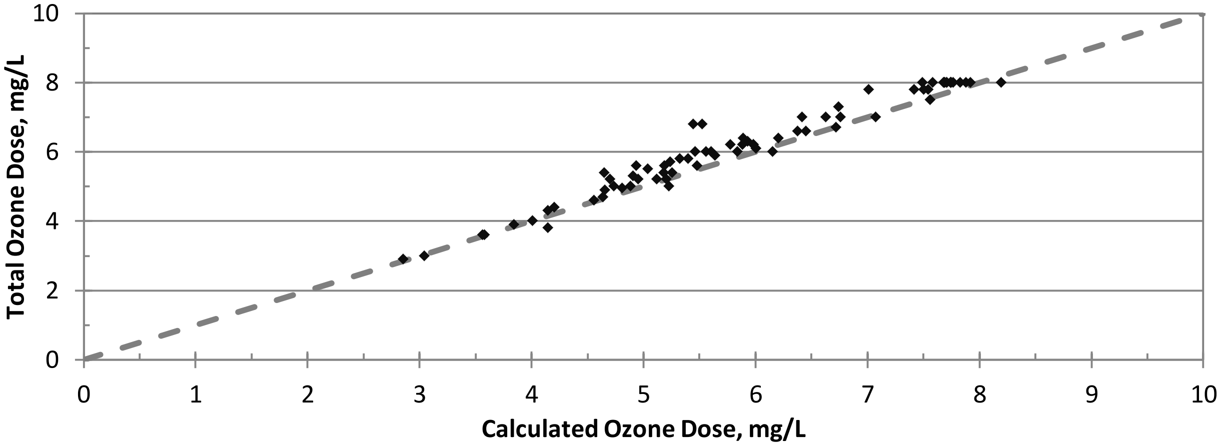


Figure 42: Total ozone dose versus calculated ozone dose

The installation of new ozone gas flow meters for this study has allowed the MWTP to more accurately know how ozone gas flow is being divided between the three sections and to calculate the sectional ozone dose. The sectional ozone dose was analyzed to determine its impact on bromate formation in each section. The minimum and maximum ozone dose applied to each section, the percent of the total ozone dose added, and the percent of bromate forming in each section is described in Table 12.

Table 12: Sectional ozone dose and bromate formation

	Units	Section 1	Section 2	Section 3
Minimum Ozone Dose	mg/L	0.7	1.0	0.4
Maximum Ozone Dose	mg/L	2.7	3.9	2.9
Percent of Total Dose (avg.)	%	31.0	42.6	26.4
Bromate Formation (avg.)	%	29.7	39.1	31.3

Results obtained from comparing the sectional ozone dose and sectional bromate formation show the percentage of the total ozone dose being applied to each section is similar to the percentage of bromate formation occurring in the same section. However, a trend between the sectional ozone dose and bromate formation in Sections 1, 2, and 3 cannot be determined from this data (Figure 43, Figure 44, and Figure 45) as it was with the total ozone dose.

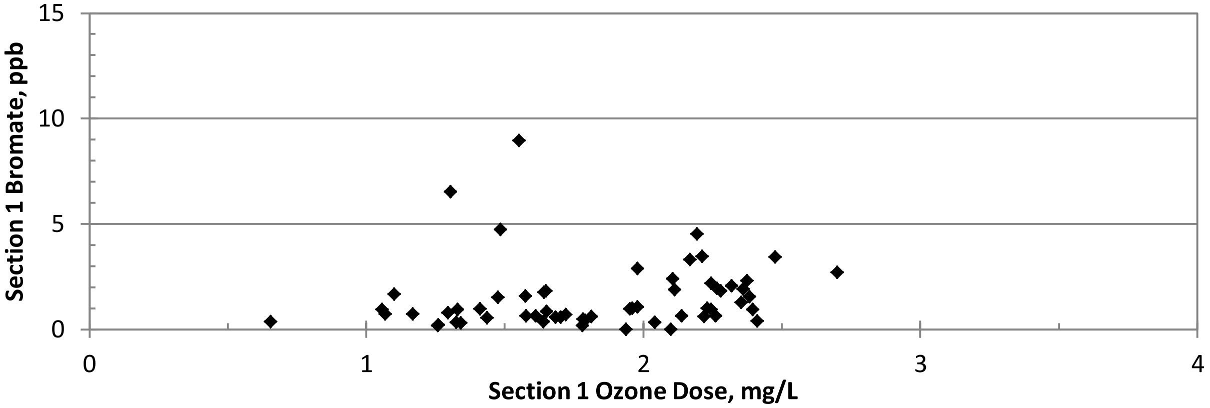


Figure 43: Section 1 bromate formation versus ozone dose

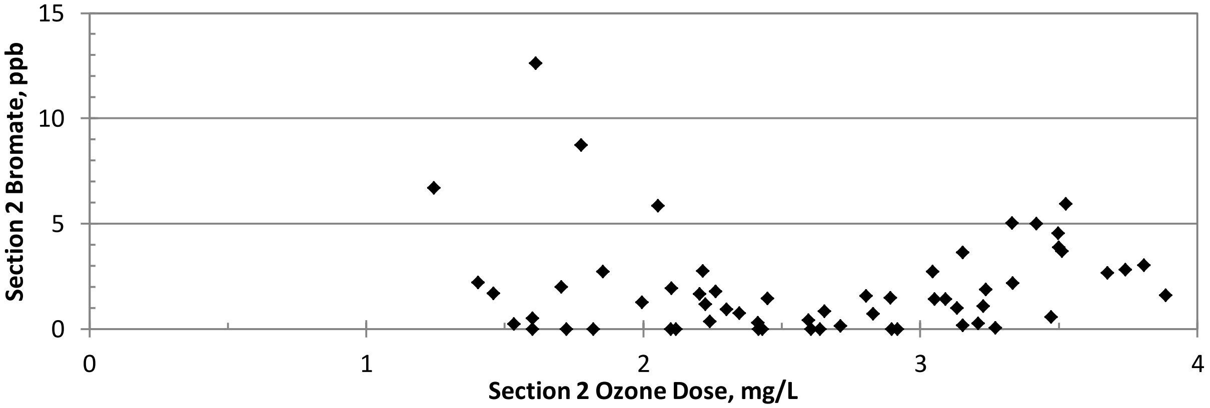


Figure 44: Section 2 bromate formation versus ozone dose

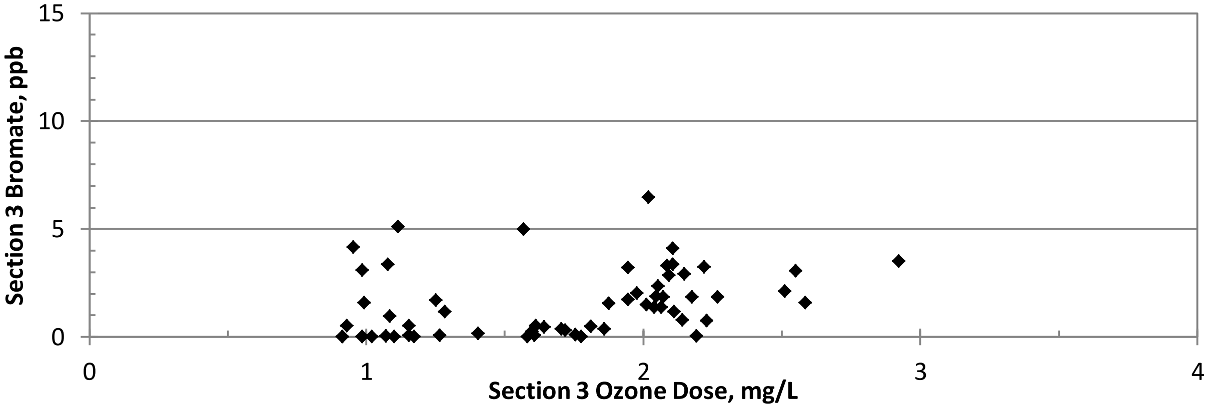


Figure 45: Section 3 bromate formation versus ozone dose

4.4.5.3. Impact of Disinfection CT Ratio on Bromate Formation

During this study, the MWTP had a goal of keeping the CT ratio (actual CT divided by the USEPA-required CT) between 1.0 and 2.0, in an effort to reduce excess ozone in the water available to oxidize bromide. The MWTP was able to keep the ozone CT ratio between 1.09 and 3.95 during this study. It can be difficult to maintain a CT ratio below the target of 2.0 when the required CT is low at higher water temperature, as described in Section 4.2.2. During this study, 57 percent of the samples were collected when the CT ratio was greater than 2.0. Out of the seven samples containing greater than 10 ppb bromate, five of them (71.4 percent) were collected when the CT ratio was above 2.5. The relationship between the ozone CT ratio and bromate formation during this study is shown in Figure 46. No trends can be determined from this data suggesting that, while it is a good operational parameter with regard to disinfection, the ozone CT ratio may not be good parameter to use for predicting bromate formation. This may be because the CT depends on two parameters, ozone residual concentration and detention time in the ozone chamber, and as these parameters change, their impact on bromate formation may be different.

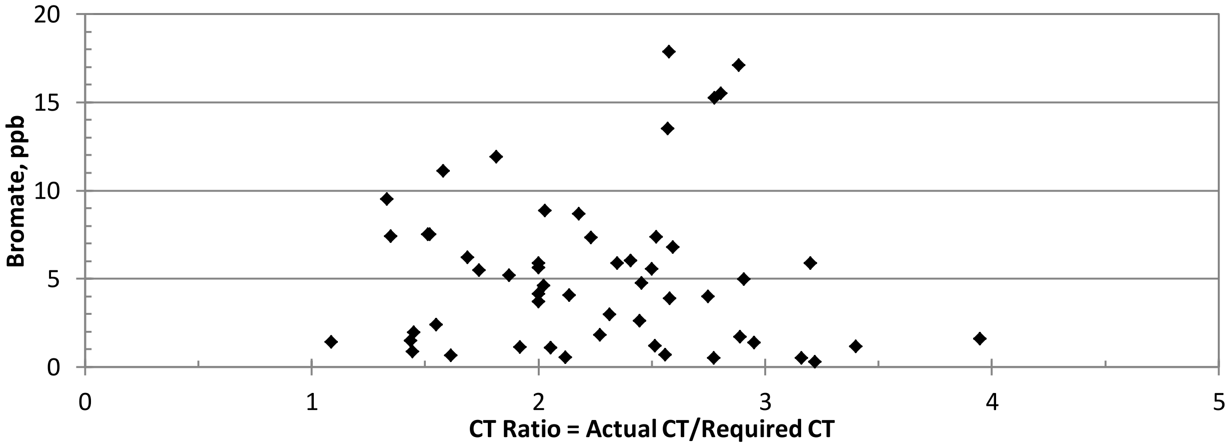


Figure 46: Bromate formation versus ozone CT ratio

4.4.6. Organics Content Measurement and Bromate Formation Impacts

Organics content is another water quality parameter known to affect the amount of bromate formation that occurs in water being treated with ozone. Literature has shown that bromate formation decreases with increasing organics content (Song et al., 1997; Siddiqui & Amy, 1993). It is suspected that this is because ozone being applied to water has a tendency to react with organics and oxidize them before reacting with bromide. This study measured organics reduction throughout the ozone chamber in an attempt to determine the impact of DOC and UV254 on bromate formation. If it can be determined that organics are oxidized differently in each section of the ozone chamber it may be possible to relate the reduction of organics to bromate formation.

4.4.6.1. Dissolved Organic Carbon

Dissolved organic carbon was analyzed in the ozone contact chamber influent, the effluent of each section, and the combined filter effluent to determine if DOC is a valuable measurement of organics reduction during ozonation and to determine how DOC impacts bromate formation. DOC was analyzed in the ozone chamber as a whole, as well as in each section. The average DOC concentration at each sample point during this study is shown Figure 47 – error bars are used to denote the standard deviation. The results show that very little DOC reduction takes place during ozonation, and a much greater concentration of DOC is removed in the MWTP filters. On average, only 7.3 percent of the ozone contact chamber influent DOC was removed during ozonation, with each chamber providing approximately equal reduction. In comparison, approximately 19 percent of the DOC in the Section 3 effluent was removed in the MWTP filters. The difference in removal rates through ozonation and biofiltration is due to partial oxidation of organics in the ozone chamber. Very little mineralization occurs during ozonation, but the increased removal through biofiltration suggests that dissolved organic matter is partially oxidized and converted to low-molecular weight compounds that can be consumed by microbes in biological filters. These findings are consistent with the literature, which determined that DOC is most often not reduced to carbon dioxide, but is converted to more biodegradable forms (Miltner et al., 1992; Siddigui & Amy, 1993).

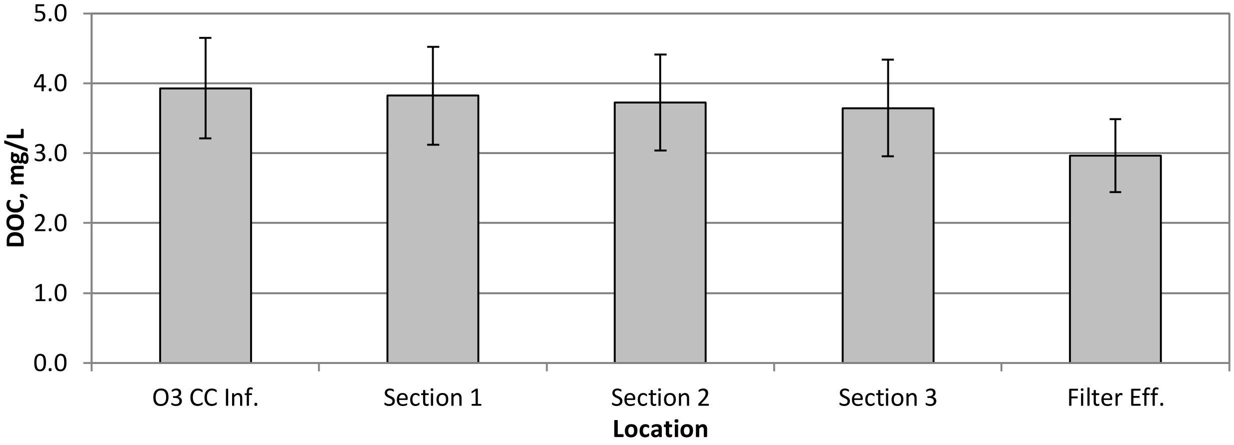


Figure 47: Average ozone contact chamber and filter effluent DOC concentration

The dissolved organic carbon concentration in the ozone contact chamber influent ranged from 2.17 to 5.44 mg/L. A loose trend of decreasing bromate formation with increasing DOC concentration is shown in Figure 48. However, three of the samples containing greater than 10 ppb bromate occurred when the DOC was between 4.29 and 4.52 mg/L, which is closer to the highest DOC concentration in the ozone contact chamber influent.

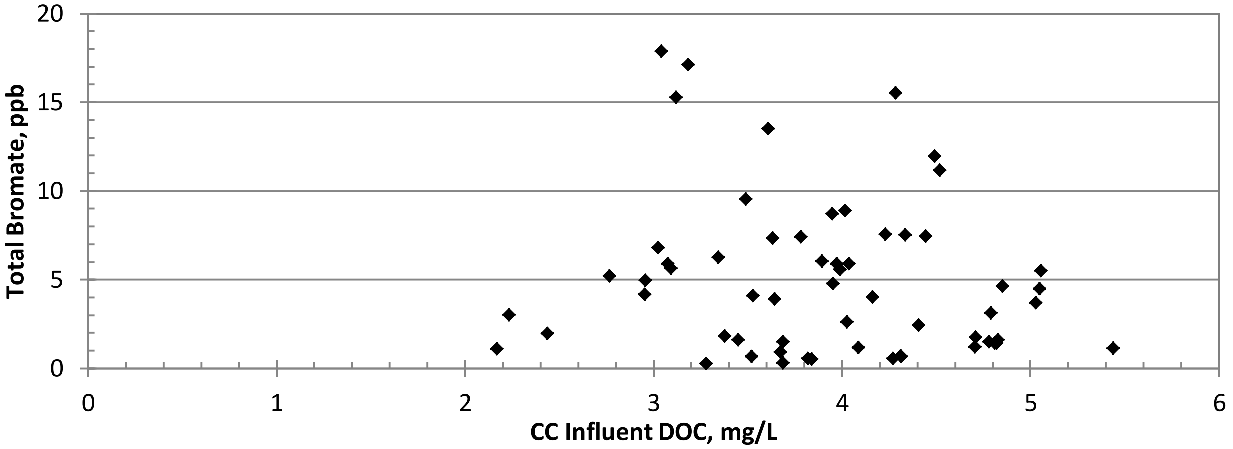


Figure 48: Total bromate formation versus contact chamber influent DOC

Analyzing the DOC in each section and comparing it to the sectional bromate formation allows correlations to be developed between the parameters on a section-by-section basis. The goal of this analysis is to determine if organics concentration impacts the ozonation process differently in the three sections. Sectional bromate formation is compared to the sectional DOC concentrations in Figure 49, Figure 50, and Figure 51, for Sections 1, 2, and 3, respectively. Sections 1 and 2 have a loose negative correlation between DOC and sectional bromate formation. Section 3 does not show any correlation between the two parameters. This indicates that ozone being applied to Sections 1 and 2 may have more of a tendency to react with dissolved organic matter in the water before reacting with bromide and that organic matter remaining in Section 3 may not be as readily oxidized. However, DOC may not be a good organics measurement to correlate to bromate formation because it is less sensitive to a total change during ozonation.

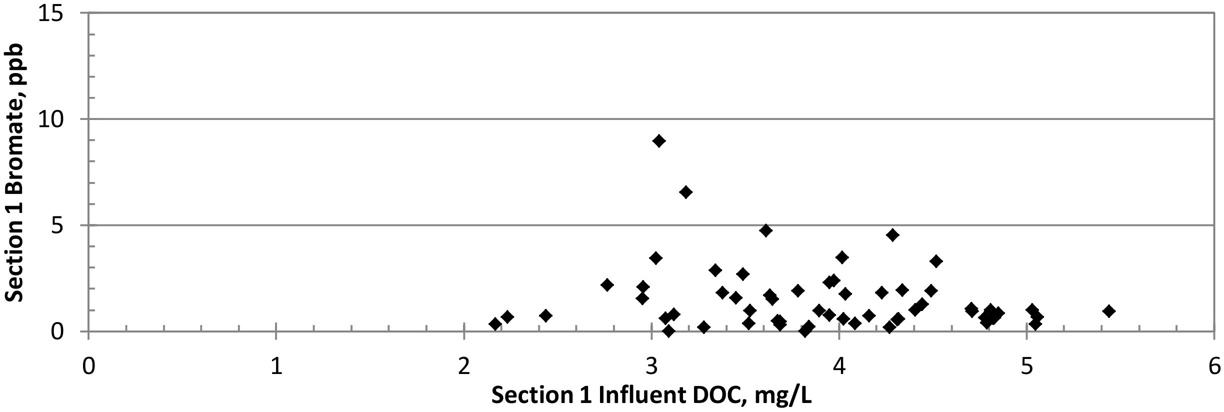


Figure 49: Section 1 bromate formation versus Section 1 influent DOC

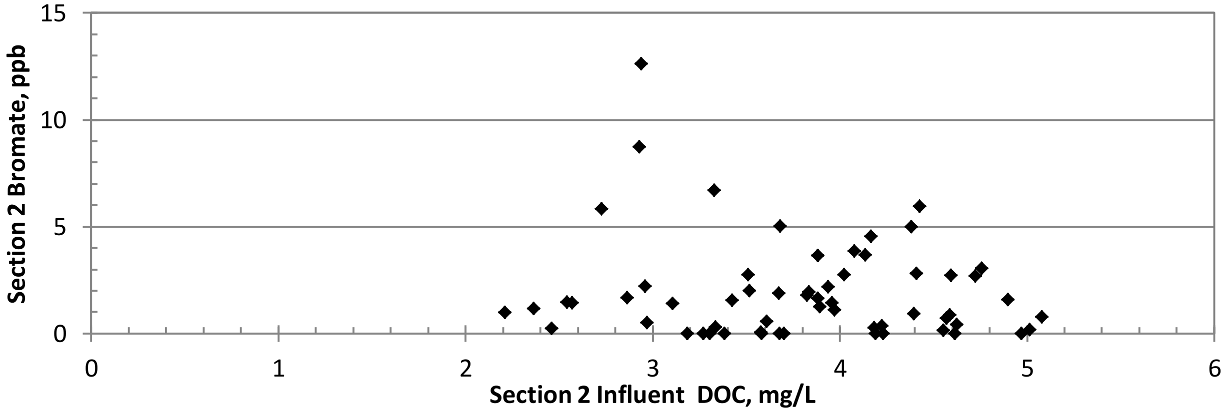


Figure 50: Section 2 bromate formation versus Section 2 influent DOC

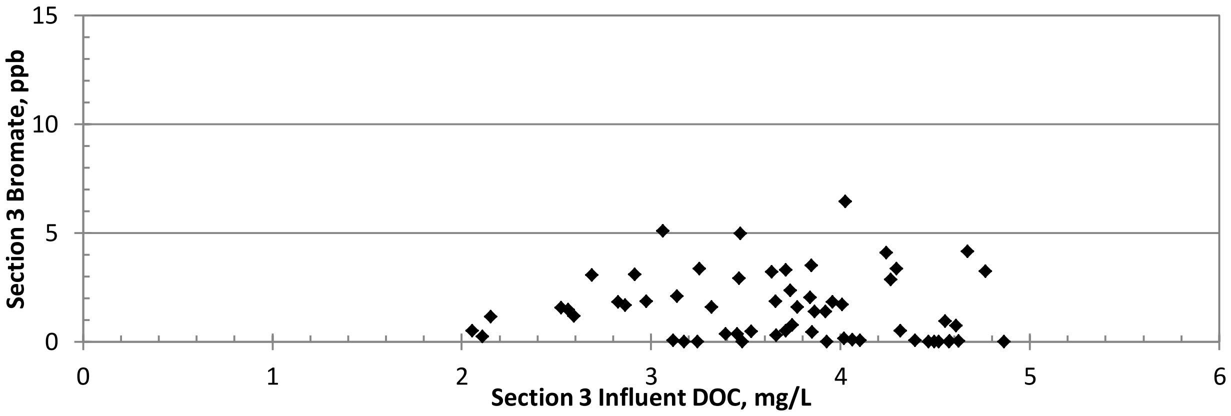


Figure 51: Section 3 bromate formation versus Section 3 influent DOC

4.4.6.2. Ultraviolet Absorbance at 254 nm

UV254 was analyzed to determine if it is a better measurement of organics oxidation than DOC during ozonation and to determine how UV254 impacts bromate formation. The previous study at the MWTP determined typical UV254 reduction in the ozone chamber, but did not determine its impact on bromate formation. The average UV254 of each sample location in this study is shown in Figure 52 – the standard deviation of each location is denoted by error bars. The data suggests that UV254 reduction takes place to a much greater extent than DOC reduction in the ozone chamber, particularly in Section 1. On average, 64.7 percent of the ozone contact chamber influent UV254 was during ozonation. Section 1 reduced approximately 50 percent of the UV254 while Sections 2 and 3 accoutned for reductions of approximately 10 and 5 percent, respectively. These results indicate that oxidation of organics decreases throughout the ozone chamber because unsaturated compounds having double or triple carbon bonds are degraded shortly after ozone is applied, and the concentration of these compounds available to be oxidized throughout the rest of the process is reduced. It is interesting to note that no UV254 reduction takes place during filtration. The lack of reduction is due to the conversion of unsaturated compounds to saturated compounds during ozonation. These saturated compounds, having single carbon bonds, do not absorb UV254 and are readily consumed during biofiltration, but are included in DOC and TOC measurements. The DOC reduction achieved during filtration in this study is attributed to the consumption of these compounds in MWTP's biological filters. These results are consistent with literature, which concluded that UV254 can be used to determine partial oxidation or destruction of aromatic NOM during ozonation (Miltner et al., 1992).

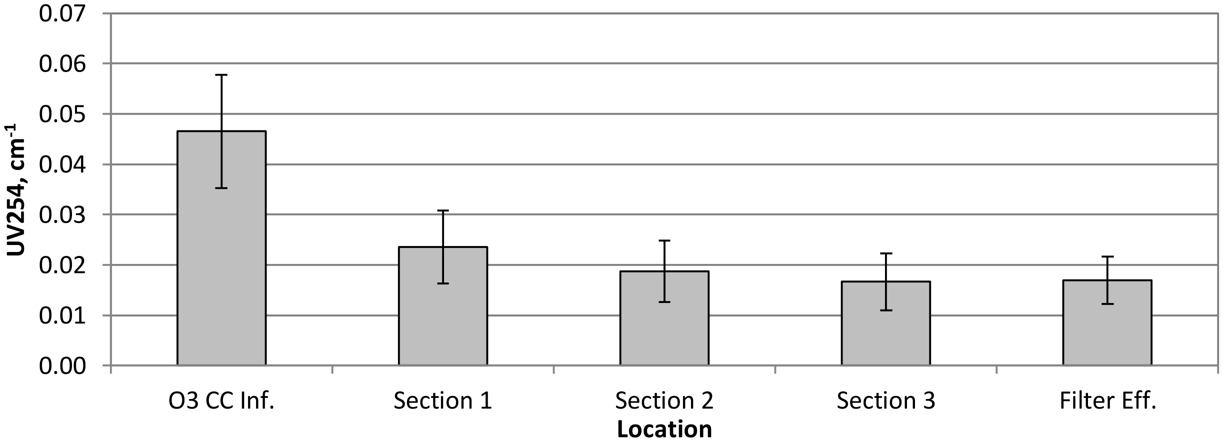


Figure 52: Average ozone chamber and filter effluent UV254

The ozone contact chamber influent UV254 ranged from 0.030 to 0.068 cm^{-1} over the sampling period. A loose trend of decreased total bromate formation with increasing UV254 is shown in Figure 53. However, three of the samples containing greater than 10 ppb bromate occurred when the UV254 was greater than 0.05 cm^{-1}. These outlier data points make it difficult to come to a definite conclusion regarding the impact of UV254, indicating that other water quality parameters also impacted bromate formation.

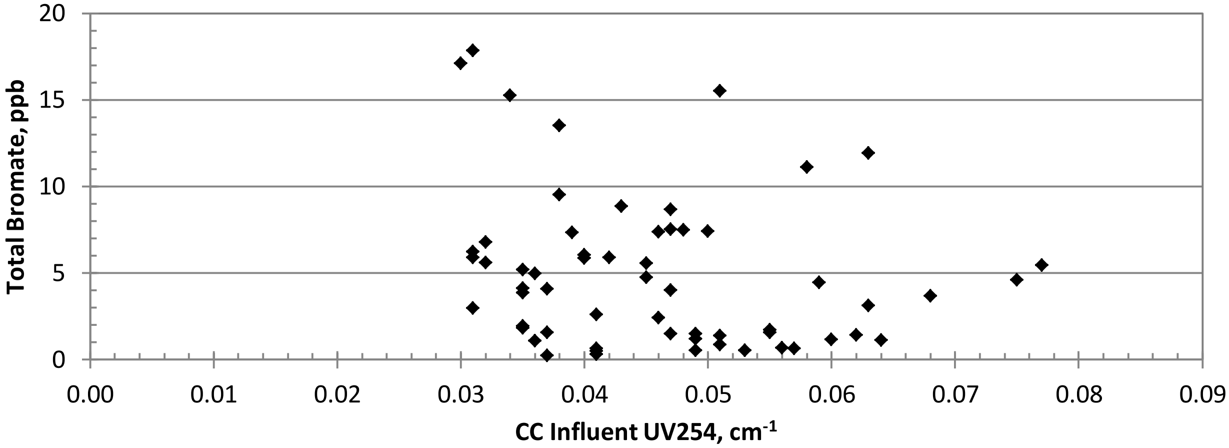


Figure 53: Bromate formation versus contact chamber influent UV254

Analyzing the UV254 in each section and calculating the sectional bromate formation allows analysis for potential correlations between bromate formation and UV254 to be determined on a section-by-section basis. Again, the goal of this analysis is to determine if dissolved organic matter impacts ozonation differently in each section. Sectional bromate formation is compared to the influent UV254 in Figure 54, Figure 55, and Figure 56 for Sections 1, 2, and 3, respectively. The data from Section 1 suggests there is a negative correlation between the sectional bromate formation and the influent UV254, with less bromate forming as the UV254 increases. The same relationship cannot be determined in Sections 2 and 3, as neither section shows a correlation between bromate formation and UV254. These findings suggest that oxidation occurring in Section 1 may have a preference towards aromatic carbons over bromide and that partially oxidized organics remaining in Sections 2 and 3 are not reduced further and do not impact bromate formation in the same way as in Section 1. Studying the impact of UV254 reduction on bromate formation will proved more answers on this topic.

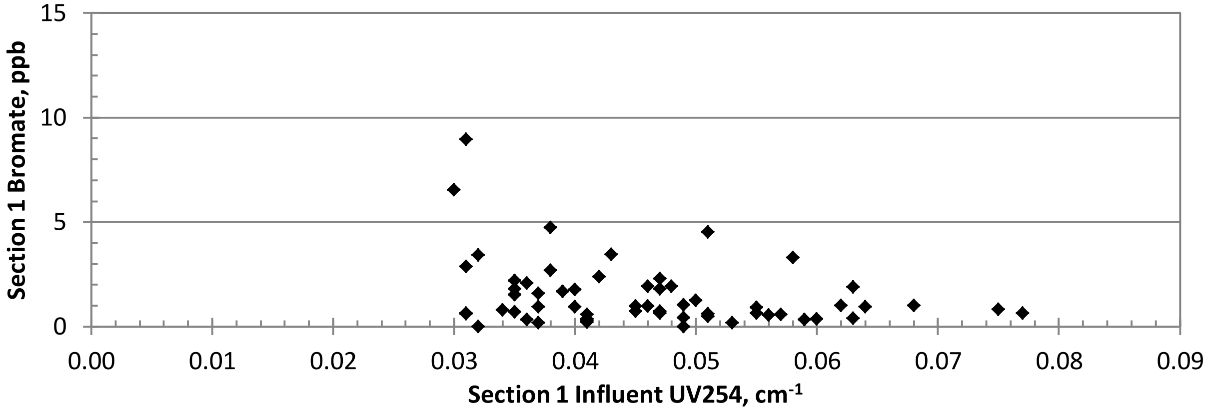


Figure 54: Section 1 bromate formation versus Section 1 influent UV254

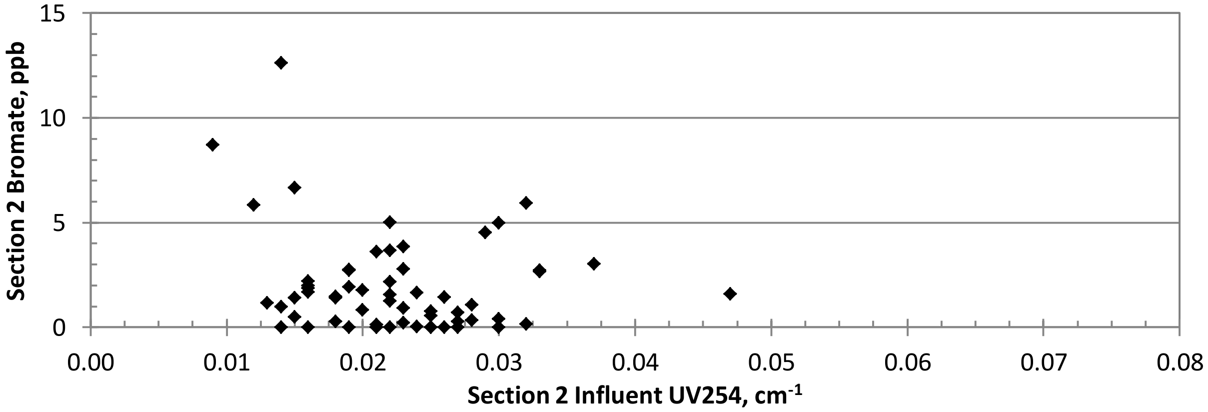


Figure 55: Section 2 bromate formation versus Section 2 influent UV254

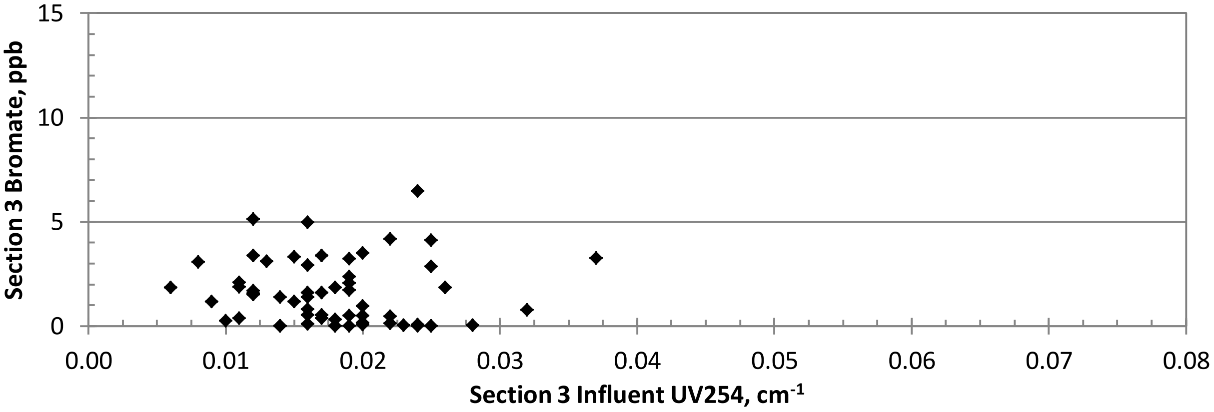


Figure 56: Section 3 bromate formation versus Section 3 influent UV254

The impact of UV254 reduction on bromate formation was studied to determine if oxidation has a preference towards reducing organic molecular structures prior to oxidizing bromide. The analysis was done by first determining if there is a relationship between the influent UV254 and UV254 reduction. The UV254 reduction was then plotted against the total bromate formation in the ozone chamber. It was determined that UV254 reduction increases linearly as influent UV254 increases, as shown in Figure 57. This finding suggests that the aromatic content of organics in the MWTP source water is relatively stable.

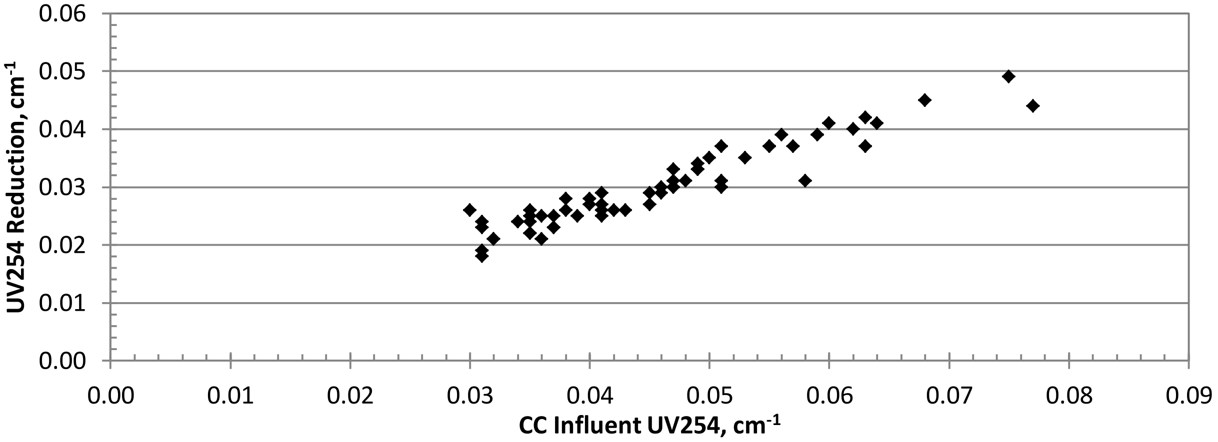


Figure 57: Ozone contact chamber influent UV254 versus UV254 reduction

UV254 reduction in the ozone chamber ranged from 0.018 to 0.049 cm^{-1} during this study. It was determined that there is a negative correlation between total bromate formation and UV254 reduction, as shown in Figure 58. The data also shows that nearly all of the samples containing greater than 10 ppb bromate occurred when UV254 reduction was lower than 0.03 cm^{-1}; recalling Figure 57 would suggest that reduction below 0.03 cm^{-1} correlates to low influent UV254 values. Similar to the impact of influent UV254 on bromate formation, UV254 reduction is negatively correlated to bromate formation in Section 1, but no trend can be determined in Sections 2 or 3.

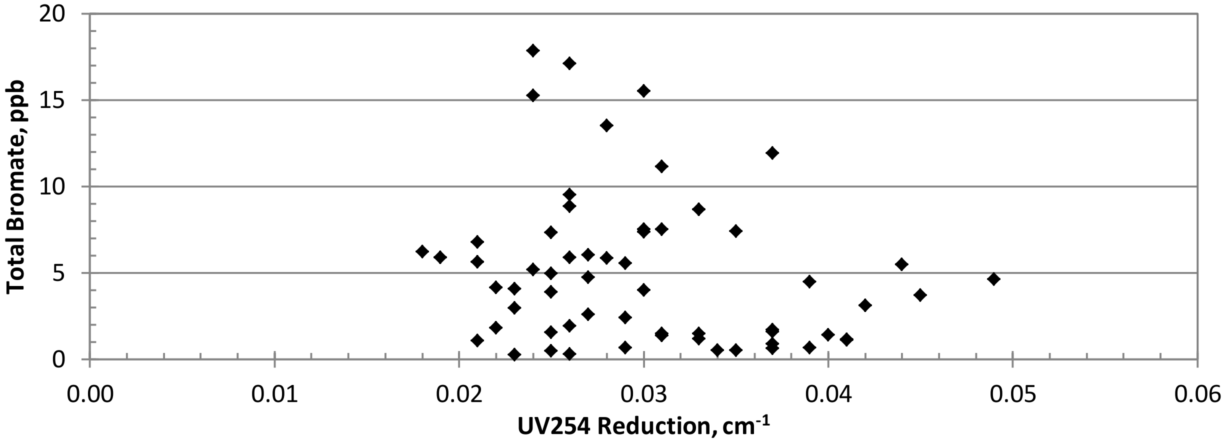


Figure 58: UV254 reduction versus total bromate formation

4.4.7. Hydraulic Retention Time

The hydraulic retention time (HRT) in the ozone chamber was calculated by dividing the volume of each section by the water flow rate through the MWTP. A summation of the sectional HRT was used to determine the total HRT in an attempt to relate it to bromate formation. The total HRT ranged from 23.1 to 46.2 minutes during this study. A loose trend showing that bromate formation increases as the total HRT increases can be seen in Figure 59. Also, 5 of the 15 samples (33 percent) collected when the total HRT was greater than 35 minutes contained more than 10 ppb bromate.

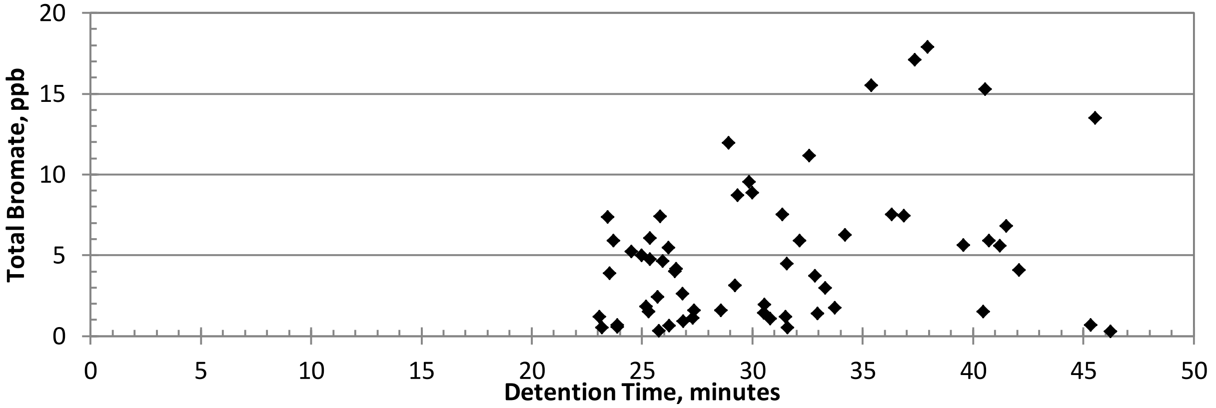


Figure 59: Bromate formation versus contact chamber HRT

Samples collected when the HRT was greater than 35 minutes had an average bromate concentration of 8.30 ppb (σ=6.03 ppb), while samples collected when the HRT was less than 35 minutes had an average concentration of 3.79 ppb (σ=3.17 ppb). Similar trends could be seen in the data from each section, suggesting that the ozonation HRT may impact bromate formation. This finding could be of particular concern to the MWTP during the summer when water demand is between 5 and 7 MGD because operation of two ozonation chambers is required. The decreased flow (one-half of the total flow) results in an increased HRT in both ozone chambers. The low HRT in the month between June 25 and July 25 is suspected to be one of the reasons bromate formation was minimal, as most of the samples collected had an HRT of 25 minutes or less, as shown in Figure 60. In comparison, the average HRT during the rest of the study was 31.5 minutes.

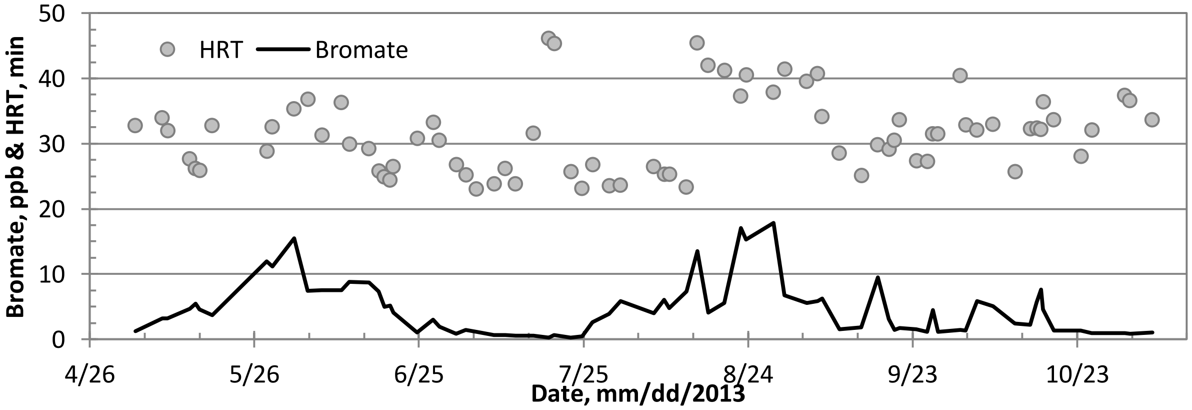


Figure 60: Comparison of bromate formation and ozonation HRT

CHAPTER 5. BROMATE PREDICTION MODEL

As described in Chapter 2, Storlie (2013) presented a bromate prediction model that defines the relationship between water quality parameters, operational controls, and bromate formation in the MWTP. The goal of creating a bromate prediction model is to eventually implement the model into the MWTP SCADA system to aid with operational control of the ozone system. An objective of this study was to determine whether or not the original bromate prediction model is representative of the results obtained during this study, and to modify or create a new model if it was not. However, some of Storlie's findings were not as impactful in this study, which affects how the model fits the current data. The differences in conclusions can be attributed to operational changes made as part of this study that create a challenge when trying to model bromate formation as a whole data set. It was suspected that the existing bromate model would need to be re-calibrated to fit the 2013 data and reflect the operational changes.

5.1. Original MWTP Bromate Prediction Model

Storlie (2013) presented a regression model to predict bromate formation in the MWTP using data from samples collected in 2012. A regression-type model was selected over other types because the MWTP already uses regression models to predict other water quality parameters. The equation of the final model selected is provided in Section 2.4.4. The model indicated that bromate formation was positively correlated to ozone dose, bromide concentration, pH, and water temperature, but was negatively correlated to TOC. Storlie's (2013) model produced a correlation coefficient of 0.78 and was able to capture day-to-day changes in bromate formation. However, the model appeared to underestimate bromate formation in the highest samples, and overestimate bromate formation in the lowest samples.

Bromate formation during this study, as predicted by the Storlie (2013) model, is presented in Figure 61. The model showed no correlation to this study's data, a result of the operational changes implemented. Also, bromate formation in 2012 was, on average, two times greater than in this study and bromate formation greater than 10 ppb occurred approximately three times more often. The differences in operational strategy and bromate formation between the two studies result in water quality parameters, or model variables, having different levels of importance.

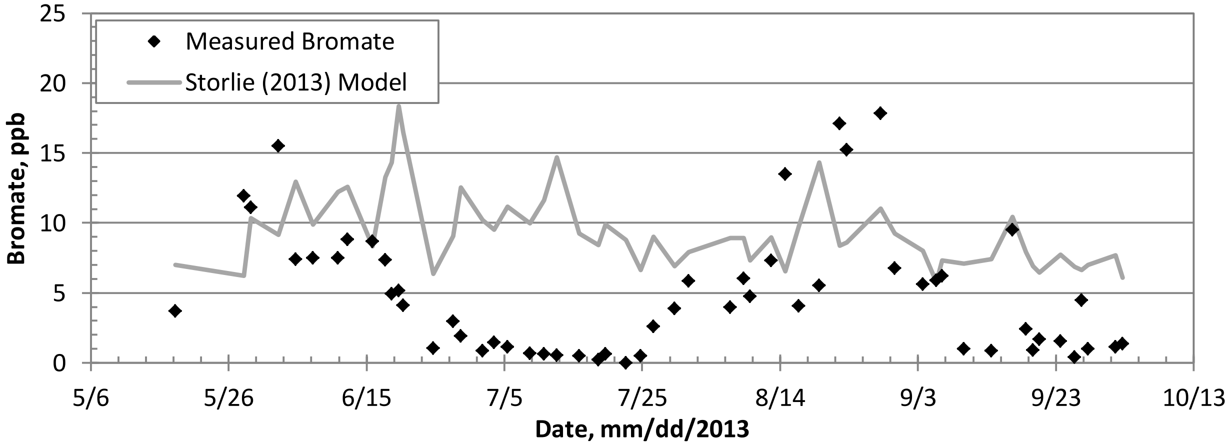


Figure 61: Storlie (2013) prediction model results

5.2. Revised MWTP Bromate Prediction Model

The original bromate prediction model had to be re-calibrated as a result of the poor correlation between the Storlie (2013) model and this study's data. The parameters shown in the general equation below were first used to refine the model; however, very poor correlation was achieved.

$$BrO_3^- = e^{-\beta_1} \times O_{3(dose)}^{\beta_2} \times DOC^{\beta_3} \times pH^{\beta_4} \times (Br^-)^{\beta_5} \times Temp^{\beta_6} \times HRT^{\beta_7} \times UV_{254}^{\beta_8}$$

Based on the results of the least-squares analysis conducted, it was determined that some of the impactful variables in the original prediction model, including TOC (DOC), water temperature, and bromide concentration did not significantly impact the model under the current operating conditions. In particular, the bromide concentration and water temperature had very little impact on bromate formation as determined through the modeling process, in large part because bromide (μ=61 ppb; σ=10 ppb; n=56) and water temperature (μ=20°C; σ=1.7°C; n=56) were held relatively constant throughout the sampling period. Also, the MWTP is most concerned with bromate formation when the water temperature is above 15°C, as determined in both 2012 and 2013, so it was decided the model would only be used above 15°C and the variable could be removed. Bromide was also removed because preliminary model calculations showed that it was not a determinant factor in bromate formation under the current operating conditions. The future combined raw water bromide concentration will remain similar to the levels of this study, as the same source water selection strategy will be used. DOC was removed from the model because UV254 was shown to be a more impactful organics measurement.

After determining that DOC, bromide, and water temperature could be removed from the model without impacting the final results, parameters that the MWTP already measures or calculates in the SCADA system were used to predict bromate formation. The regression model that best fit the results of this study is shown below. Ozone dose, pH, and hydraulic residence time were determined to have a positive impact, while ammonia and UV254 were determined to have a negative impact on bromate formation. Overall, ozone dose had the greatest impact on bromate formation.

$$\mathrm{BrO_3^-} = e^{-12.562} \times \mathrm{O}_{3,\ \mathrm{dose}}^{2.070} \times \mathrm{pH}^{0.105} \times \mathrm{NH}_3^{-0.265} \times \mathrm{HRT}^{1.220} \times \mathrm{UV}_{254}^{-1.722}$$

The bromate prediction model for this study produced a correlation coefficient of only 0.36, which is likely due to the low levels of bromate that formed. Samples containing greater than 10 ppb and less than 2.0 ppb bromate were not accurately described by the model, as reflected in Figure 62. Although the model may not yet be able to be used for operational control, it is able to determine which water quality parameters and operational controls are most impactful in relation to the other parameters that could not be done on an individual basis. The model results suggest that not all water quality parameters impact bromate formation equally. Ozone dose was shown to have the greatest positive correlation to bromate formation, and its impact could potentially be reduced further by adding Section 1 to the MWTP CT calculation, as described in Chapter 6.

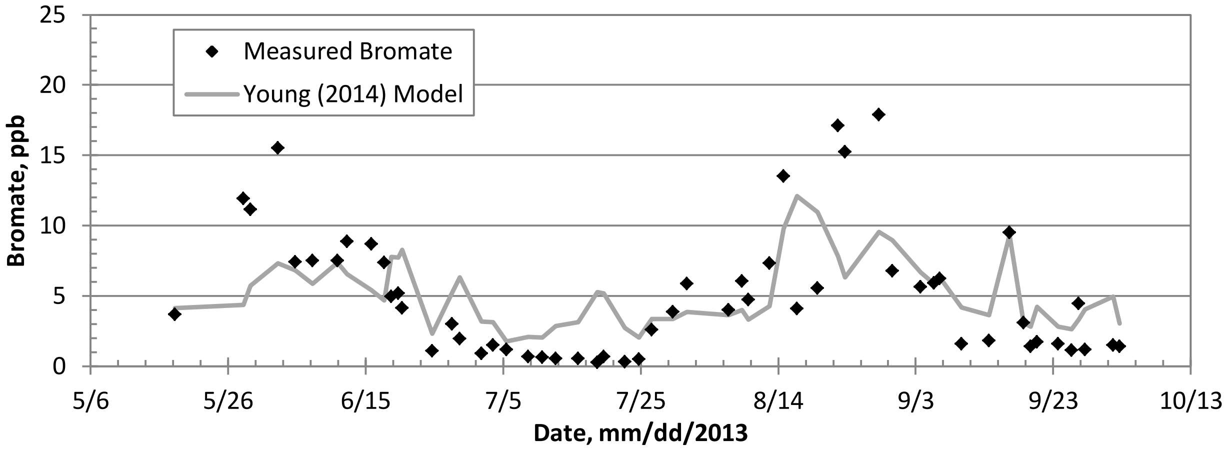


Figure 62: 2013 bromate formation model results

The next step in the modeling process could be to combine results from the two studies, as well as future samples collected to develop a model for all of the data. This strategy would provide model results over a wider range of operational conditions and could potentially lead to more accurate results. However, the data from 2012 may not be able to be combined with current data because of differences in operational strategy. Also, with sectional ozone gas flow data, it may be possible to develop a section-by-section bromate formation model.

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

The purposes of this study were to develop and implement operational changes to minimize bromate formation in the MWTP, and to gain a better understanding of factors that affect bromate formation during ozonation. The previous study conducted at the MWTP determined that bromate formation is a legitimate concern and recommended that operational changes be made to reduce the formation. Results from this study show that bromate formation has been greatly reduced as a result of the operational changes made.

6.1. Conclusions

Many conclusions may be drawn from the results of this study, with some agreeing with the findings of Storlie (2013), and some conflicting with the findings of that study. Conflicting conclusions between the studies may be attributed to changes in operational strategy at the MWTP. The major conclusions of this study are as follows:

- Source water bromide concentrations were verified. The Moorhead Aquifer contains approximately 4.4 times more bromide than the Buffalo Aquifer and 5.3 times more than the Red River. Eliminating use of the Moorhead Aquifer during the summer reduced the influent bromide concentration by approximately 35.3 percent when compared to the Storlie (2013) study.
- Source water ammonia concentrations were quantified. The Moorhead Aquifer (μ=1.33 mg/L) contains the most ammonia, followed by the South Buffalo wells (μ=0.71 mg/L), North Buffalo wells (μ=0.31 mg/L), and Red River (μ=0.02 mg/L). This information is important to the MWTP because it is related to the conclusion that ammonia is negatively correlated to bromate formation and could help determine an ammonia dose based on the source water selection.
- The operational changes made in the MWTP for this study were effective, and bromate formation was greatly reduced. Only 9.3 percent of samples contained more than 10 ppb bromate, compared to 38.9 percent in 2012. Only two finished

water samples contained more than 10 ppb bromate. The average bromate concentration was reduced from 9.7 (2012) to 4.5 ppb (2013).

  - Approximately 39 percent of the total bromate formation occurs in Section 2. Section 3 and Section 1 formed approximately 31 percent and 30 percent, respectively.
- Bromate did not form over 10 ppb when the water temperature was below 16.4°C. This agreed with the findings of Storlie (2013).
- The total ozone dose had a positive correlation to bromate formation; however, the sectional ozone dose could not be correlated to bromate formation.
  - The sectional ozone dose can be accurately calculated using the new ozone gas flow meters.
  - Although the CT ratio is a useful indicator disinfection compliance, it could not be correlated to bromate formation.
- There is a loose negative trend between the DOC concentration and bromate formation in the ozone chamber influent and Sections 1 and 2. However, a trend could not be determined in Section 3.
  - The DOC concentration does not change considerably during ozonation.
- There is a loose negative trend between the ozone chamber influent UV254 and bromate formation.
  - UV254 more negatively impacts bromate formation in Section 1 than in Sections 2 and 3, suggesting that ozone may be used to break down UV254 absorbing compounds more readily in Section 1.
  - UV254 is reduced by approximately 65 percent during ozonation, with approximately 50 percent of the reduction taking place in Section 1.
- The bromate prediction model presented by Storlie (2013) was modified to simulate this study's results. Ozone dose, pH, ammonia, hydraulic retention time, and UV254 were the most impactful water quality parameters based on the model calculations.

- The combined raw water influent bromide concentration was relatively constant (μ=61 ppb; σ=10 ppb; n=56) when the Moorhead Aquifer was not used. As a result, bromide acted as a constant variable and was removed from the model.
- pH has a slight positive correlation to bromate formation throughout the entire ozone chamber because of its impact on HOBr/BrO^- equilibrium.
- Ammonia has a slight negative correlation to bromate formation.
- The hydraulic residence time during ozonation has a positive correlation to bromate formation.

6.2. Recommendations and Future Work

Although the MWTP is confident in its ability to meet regulatory standards based on the reduction in bromate formation achieved, the conclusions of this research suggest there is room for improvement regarding operation of the ozonation system and understanding bromate formation. Operationally, the strategy of eliminating the Moorhead Aquifer as a water source during the summer months should be continued, as it greatly reduces the influent bromide concentration. The MWTP should also use a maximum target CT ratio of 2.0 because it reduces the amount of excess ozone in the water. Additionally, the Minnesota Department of Health should be contacted to determine the possibility of altering the current ozone CT calculation. If Section 1 would be awarded disinfection credit, the MWTP would be able to reduce the ozone dose required for disinfection, resulting in an even further reduction in the amount of ozone available for bromate reactions. The MWTP should also continue adding ammonia prior to ozonation with a target concentration of 0.30 mg/L. To do this, they should improve the current process by installing an additional ammonia feed pump that could apply an accurate pre-ozonation ammonia dose.

Sampling of the ozone chamber should be continued to increase the amount of bromate formation data under the current operating conditions. The extra data could be used to improve the accuracy of the bromate prediction model presented in this study by modeling data that spans multiple years and a wider range of operating conditions. The feasibility of using a chemical model, utilizing reaction rates and concentrations, should also be investigated. Knowledge of bromate formation on a sectional basis could also be improved by developing a section-by-section formation model that could more accurately predict bromate formation.

6.2.1. Revised CT Calculation

As stated in Chapter 2, the MWTP uses a very conservative approach when calculating the primary disinfection credit it receives from ozone. This approach is the result of three conditions: (1) a conservative required CT equation is programmed into the MWTP SCADA system, (2) the ozone system is operated at a conservative CT ratio of approximately two times greater than required, and (3) the CT is only calculated for Sections 2 and 3. Although these strategies work well for operational control, the combined effect is that more ozone is added to the water than what is required for disinfection, potentially increasing the amount of bromate that forms in the ozone chamber. A strategy that may decrease the amount of ozone added to the water is to include Section 1 in the disinfection CT calculation.

Section 1 was originally designed for taste and odor control at high pH values. At high pH, dissolved ozone is converted to the hydroxyl free radical, which is highly reactive and has a short half-life. As a result, the ozone residual in Section 1 was expected to be negligible. After Section 1 was modified to operate at a lower pH during the summer, less hydroxyl radical forms and the residual ozone concentration may be monitored. It is recommended to investigate the potential for including Section 1 in the ozone disinfection CT calculation. This change would require review and approval by the Minnesota Department of Health, as it has a direct impact on the MWTP disinfection process. The new CT calculation proposed by this study is as follows:

$$\text{Proposed CT (mg/L·min)}=0.7\left[C_1\left(\frac{V_1}{Q}\right)+C_2\left(\frac{V_2}{Q}\right)+C_3\left(\frac{V_3}{Q}\right)\right]$$

The proposed CT, which was calculated using the ozone residual and HRT in each section, is compared to the current CT in Figure 63. The deviation between the dashed line and diamond markers represents an additional gain in CT. The data shows that when Section 1 was included in the CT calculation there was an average gain of 0.22 mgL^{-1}min (σ=0.20 mgL^{-1}min) in the CT being achieved. When analyzed in terms of the CT ratio, which can be correlated to the amount of excess ozone available in the ozone chamber, the proposed CT calculation increased the average ratio from 2.37 to 2.96, a 24.5 percent increase.

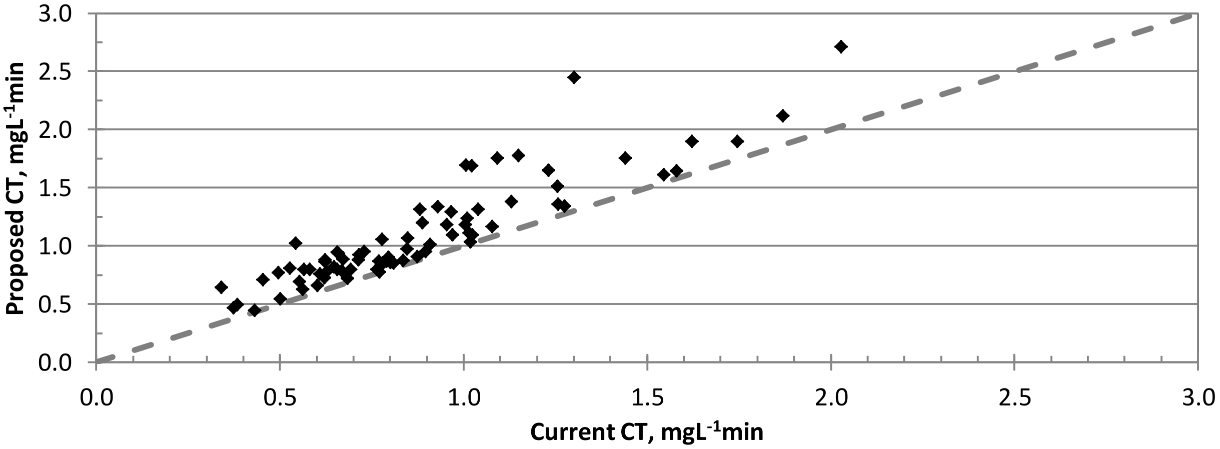


Figure 63: Proposed CT calculation versus current CT calculation

If the MDH would award Section 1 disinfection credit the benefits may be two-fold. First, the ozone dose required may be reduced because of the additional residual used in the CT calculation. This would reduce MWTP's operational cost for the ozonation process, as less ozone would be generated on a daily basis. More importantly, the reduced ozone dose could potentially reduce bromate formation even further than already achieved, resulting in higher quality water.

6.2.2. Ammonia Feed System Modification

Although it has been proven that ammonia reduces bromate formation in ozonation systems (Song et al., 1997; Williams et al., 2003; Hofmann & Andrews, 2007; von Gunten, 2003; AWWA & ASCE, 2012), the results of this study are not conclusive. The MWTP should modify its ammonia feed system to allow for a more accurate pre-ozonation dose to be added. Ammonia is currently added to the ozone chamber influent by adjusting a manually-operated ball valve to “steal” ammonia flow from the main feed point in the clearwell. This method does not allow an exact ammonia dose to be fed. The MWTP would need to purchase very few ball valves and a static mixer to modify the existing process in a manner that would allow for separate ammonia feed points. Connecting the chemical feed pump to the SCADA system would allow the pump to be adjusted automatically based on the plant flow rate and desired ammonia dose. The bromate study could then continue and the impact of ammonia could be studied more accurately because the ammonia concentration would be controlled more effectively.

REFERENCES

APHA, AWWA, WEF. (2005). *Standard Methods for the Examination of Water & Wastewater.* Washington, DC.: American Public Health Association, American Water Works Association, Water Environment Federation.

Arvai, A., Jasim, S., & Biswas, N. (2012). Bromate Formation in Ozone and Advanced Oxidation Processes. *Ozone Science and Engineering, 34*, 325-333.

AWWA & ASCE. (2012). *Water Treatment Plant Design, Fifth Edition.* (S. Randtke, & M. Horsley, Eds.) Chicago: McGraw-Hill.

Elovitz, M., & von Gunten, U. (1999). Hydroxyl Radical/Ozone Ratios During Ozonation Process. I. The Rct Concept. *Ozone Science & Engineering, 21*, 239-260.

Elovitz, M., von Gunten, U., & Kaiser, H. (2000). Hydroxyl Radical/Ozone Ratios During Ozonation Processes. II. The Effect of Temperature, pH, Alkalinity, and DOM Properties. *Ozone Science and Engineering, 22*, 123-150.

Galey, C., Dile, V., Gatel, D., Herremans, L., & Cavard, J. (2004). Impact of Water Temperature on Resolving the Challenge of Assuring Disinfection While Limiting Bromate Formation. *Ozone Science and Engineering, 26*(3), 247-256.

Galey, C., Gatel, D., Amy, G., & Cavard, J. (2000). Comparative Assessment of Bromate Control Options. *Ozone Science & Engineering, 22*(3), 267-278.

Galey, C., Mary-Dile, V., Gatel, D., Amy, G., & Cavard, J. (2001). Controlling Bromate Formation. *Journal AWWA, 93*(8), 105-115.

Glaze, G., Weinberg, H., & Cavanagh, J. (1993). Evaluating the Formation of Brominated DBPs During Ozonation. *Journal AWWA, 85*(1), 96-103.

Guo, Z., Pei, Y., Yang, M., Zhang, Y., Zhang, J., Fan, J., & Hirotsuji, J. (2007). Removal of organics and control of bromate for a southern China water supply. *Journal AWWA, 99*(10), 110-116.

Haag, W., & Hoigne, J. (1983). Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromate. *Environmental Science Technology, 17*, 261-267.

Hautman, D. P., & Munch, D. J. (1997). *Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography.* Cincinnati, OH: USEPA.

Hofmann, R. (2000). *Using Ammonia to Inhibit Bromate Formation During Ozonation.* PhD Thesis, University of Toronto, Department of Civil Engineering.

Hofmann, R., & Andrews, R. (2001). Ammoniacal Bromamines: A Review of Their Influence on Bromate Formation During Ozonation. *Water Research, 35*(3), 599-604.

Hofmann, R., & Andrews, R. (2007). Potential side effects of using ammonia to inhibit bromate formation during the ozonation of drinking water. *Journal of Environmental Engineering & Science, 6*, 739-743.

James M. Montgomery Consulting Engineers, Inc. (1992). Construction of Water Treatment Plant Expansion. *III - Contract Drawings*.

Jurenka, B. (2009, August 30). DBP: Bromate Fact Sheet. US Department of the Interior Bureau of Reclamation.

Krasner, S. W., Glaze, W. H., Weinberg, H. S., Daniel, P. A., & Najm, I. N. (1993). Formation and Control of Bromate During Ozonation of Waters Containing Bromide. *Journal AWWA, 85*(1), 73-81.

Langlais, B., Reckhow, D., & Brink, D. (1991). *Ozone in Water Treatment: Application and Engineering.* Chelsea, MI: Lewis Publishers: Cooperative Research Report, AwwaRF and Compagnie Generale des Eaux.

Legube, B., Parinet, B., Gelinet, K., Berne, F., & Croue, J. (2004). Modeling of bromate formation by ozonation of surface waters in drinking water treatment. *Water Research, 38*, 2185-2195.

Miltner, R., Shukairy, H., & Summers, R. (1992). Disinfection By-Product Control by Ozonation and Biotreatment. *Journal AWWA, 84*(11), 53-62.

Moorhead Public Service. (2011). *Standard Operating Procedures Manual & Quality Assurance Manual.* Moorhead, MN.

Moorhead Public Service. (2013). *Wellhead Protection Plan. Part II.* Moorhead, MN.

Neemann, J., Hulsey, R., Rexing, D., & Wert, E. (2004). Controlling Bromate Formation During Ozonation with Chlorine and Ammonia. *Journal AWWA, 96*(2), 26-28.

Pontius, F. W., & Diamond, W. R. (1999). Complying With the Stage 1 D/DBP Rule. *Journal AWWA, 91*(3), 16-32.

Portlock, D. (2012). *A Comparative Study of Nitrification in Fargo and Moorhead Water Distribution Networks.* M.S. Thesis, North Dakota State University of Agriculture and Applied Science, Department of Civil Engineering.

Potter, B. B., & Wimsatt, J. C. (2003). *Method 415.3: Determination of Total Organic Carbon and Specific UV Absorbance at 254nm in Source Water and Drinking Water.* Cincinnati, OH: US EPA.

Rakness, K. (2005). *Ozone in Drinking Water Treatment: Process Design, Operation, and Optimization* (First ed.). (M. Kozyra, Ed.) Denver: American Water Works Association.

Siddiqui, M. S., & Amy, G. L. (1993). Factors Affecting DBP Formation During Ozone-Bromide Reactions. *Journal AWWA, 85*(1), 63-72.

Song, R., Westerhoff, P., Minear, R., & Amy, G. (1997). Bromate minimization during ozonation. *Journal AWWA, 89*(6), 69-78.

Soule, R. (2012). *Amended Wellhead Protection Plan. Part I.* Minnesota Department of Health.

Storlie, L. (2013). *An Investigation Into Bromate Formation in Ozone Disinfection Systems.* M.S. Thesis, North Dakota State University of Agriculture and Applied Science, Department of Civil Engineering.

Symons, J. M., & Zheng, M. C. (1997). Technical note: Does hydroxyl radical oxidize bromide to bromate? *Journal AWWA, 89*(6), 106-109.

USEPA. (1999). *EPA Guidance Manual: Disinfection Profiling and Benchmarking.* Washington, D.C.: Office of Water.

USEPA. (2001). *Stage 1 Disinfectants and Disinfection Byproducts Rule: A Quick Reference Guide.* Washington DC: Office of Water.

von Gunten, U. (2003). Ozonation of drinking water: Part II. Disinfection and by-product formation in the presence of bromide, iodide or chlorine. *Water Research, 37*, 1469-1487.

von Gunten, U., & Hoigne, J. (1994). Bromate Formation During Ozonation of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions. *Environmental Science and Technology, 28*, 1234-1242.

Wagner, H. P., Pepich, B. V., Pohl, C., Srinivasan, K., De Borba, B., Lin, R., & Munch, D. J. (2009). *Method 302.0: Determination of Bromate in Drinking Water Using Two-Dimensional Ion Chromatography with Suppressed Conductivity Detection.* Cincinnati, OH: USEPA.

Westerhoff, P., Song, R., Amy, G., & Minear, R. (1998). NOM's role in bromine and bromate formation during ozonation. *Journal AWWA, 89*(11), 82-94.

Williams, M., Coffey, B., & Krasner, S. (2003). Evaluation of pH and Ammonia for Controlling Bromate Formation during Cryptosporidium Disinfection. *Journal AWWA, 95*(10), 82-93.

APPENDIX

Table A 1: Sample pH and Temperature

Date	pH					Temperature				
	O_3 CC In.	S-1	S-2	S-3	Res.	O_3 CC In.	S-1	S-2	S-3	Res.
mm/dd/yy						ºC				
5/4/13 6:30 AM	11.30	10.91	9.73	9.70	9.48	10.0	9.9	9.8	9.7	9.7
5/9/13 5:00 AM	10.96	10.17	9.58	9.55	9.20	12.0	13.0	12.7	12.7	12.7
5/10/13 5:00 AM	10.95	10.06	9.34	9.20	9.25	13.3	14.0	14.0	14.0	14.0
5/14/13 5:15 AM	11.03	8.96	8.79	8.68	9.23	14.6	15.8	16.1	16.0	15.3
5/15/13 5:30 AM	10.93	9.11	8.95	8.89	9.21	15.5	16.5	16.5	16.4	16.0
5/16/13 12:00 AM	10.97	9.14	8.87	8.78	9.23	16.3	17.1	17.1	17.1	17.1
5/18/13 6:30 AM	11.03	9.05	8.94	8.82	9.25	16.7	18.1	18.2	18.0	17.4
5/28/13 6:00 AM	11.11	9.50	9.49	9.45	9.29	16.4	17.9	18.1	17.9	17.9
5/29/13 6:00 AM	11.03	9.60	9.52	9.49	9.29	16.6	17.7	17.5	17.6	17.6
6/2/13 5:30 AM	11.20	9.42	9.37	9.33	9.34	16.7	18.2	18.1	18.2	18.6
6/4/13 6:00 PM	10.97	9.34	9.36	9.32	9.24	16.8	17.4	17.2	17.2	18.7
6/7/13 6:45 AM	10.97	9.37	9.40	9.36	9.28	18.1	17.5	17.4	17.6	17.2
6/10/13 9:00 PM	10.98	9.22	9.19	9.13	9.24	19.4	19.8	19.7	19.6	19.7
6/12/13 7:00 AM	10.95	9.29	9.16	9.10	9.25	19.8	20.4	20.4	20.4	19.7
6/15/13 9:00 PM	11.04	9.23	8.96	8.90	9.31	21.2	21.8	21.7	22.2	21.3
6/17/13 4:30 PM	10.92	9.24	9.24	9.20	9.20	21.8	22.3	22.2	22.2	22.0
6/18/13 4:30 PM	10.95	9.49	9.44	9.41	9.09	20.0	20.4	20.4	20.3	21.7
6/19/13 5:00 PM	10.90	9.72	9.57	9.54	9.31	20.2	20.5	20.6	20.4	21.0
6/20/13 7:30 AM	10.84	9.65	9.52	9.46	9.26	20.3	20.2	20.3	20.4	20.5
6/24/13 5:10 PM	11.10	9.90	9.68	9.65	9.26	18.3	18.3	18.2	18.2	19.8
6/27/13 2:30 PM	11.10	9.66	9.63	9.58	9.29	19.3	19.2	19.2	19.2	19.9
6/28/13 4:30 PM	10.83	9.69	9.66	9.64	9.28	19.7	20.1	20.3	20.3	20.7
7/1/13 8:00 PM	10.71	9.28	8.99	8.93	9.23	21.5	21.7	21.7	21.7	21.0
7/3/13 1:00 PM	10.96	9.26	9.16	9.10	9.32	21.4	21.7	21.6	21.6	21.8
7/5/13 11:45 AM	10.84	9.05	9.08	8.98	9.33	21.7	22.1	21.9	22.1	22.6
7/8/13 4:30 PM	10.81	9.08	8.89	8.81	9.29	21.9	22.2	22.2	22.3	21.6
7/10/13 5:35 PM	10.74	9.19	9.03	8.93	9.30	21.7	21.9	21.9	21.9	22.5
7/12/13 2:30 PM	11.00	9.20	8.97	9.00	9.30	22.4	22.3	22.4	22.5	23.0
7/15/13 8:45 PM	10.60	9.34	9.14	9.09	9.33	20.8	19.6	19.6	20.1	22.6
7/18/13 3:45 PM	11.06	9.53	9.43	9.32	9.35	21.4	21.2	21.1	21.1	21.6
7/19/13 3:45 PM	11.20	9.14	9.08	9.07	9.33	21.6	22.4	22.4	22.3	21.8
7/22/13 4:00 PM	10.92	8.97	8.96	8.91	9.28	20.6	20.1	20.3	20.6	21.9
7/24/13 5:30 PM	11.17	9.10	9.02	8.99	9.30	20.3	20.1	20.1	20.3	21.7
7/26/13 3:15 PM	10.97	9.22	9.04	9.01	9.28	19.8	19.7	19.4	19.9	20.3
7/29/13 4:30 PM	10.94	8.92	9.09	9.06	9.31	20.4	20.5	20.4	20.5	20.5
7/31/13 5:00 PM	10.90	9.24	9.12	9.08	9.31	20.5	20.7	20.6	20.5	20.3
8/6/13 7:00 PM	10.97	9.26	9.18	9.17	9.33	20.1	20.3	20.2	20.1	20.8
8/8/13 5:30 PM	11.04	9.38	9.35	9.29	9.32	20.3	20.5	20.6	20.1	20.5

Table A 1: Sample pH and Temperature (continued)

	pH					**Temperature**				
Date	**O_3 CC In.**	**S-1**	**S-2**	**S-3**	**Res.**	**O_3 CC In.**	**S-1**	**S-2**	**S-3**	**Res.**
mm/dd/yy						**°C**				
8/9/13 3:15 PM	10.98	9.39	9.28	9.25	9.32	20.1	19.8	20.4	20.0	19.8
8/12/13 6:00 PM	11.02	9.35	9.36	9.32	9.33	21.1	21.7	21.8	21.2	20.3
8/14/13 6:10 PM	10.90	9.33	9.22	9.18	9.28	21.4	21.5	21.8	21.4	21.8
8/16/13 5:00 PM	10.81	9.37	9.28	9.23	9.32	21.3	20.9	20.9	20.8	20.9
8/19/13 5:00 PM	10.87	9.44	9.20	9.14	9.30	22.9	22.2	22.2	22.1	21.5
8/22/13 4:30 PM	10.93	9.42	9.33	9.31	9.37	22.6	22.9	22.8	22.1	21.8
8/23/13 4:20 PM	10.81	9.41	9.33	9.31	9.28	22.4	22.6	22.6	22.1	22.9
8/28/13 3:00 PM	10.80	9.56	9.50	9.45	9.34	22.1	22.9	22.8	22.0	21.9
8/30/13 3:25 PM	10.83	9.24	9.17	9.13	9.28	22.3	22.9	22.8	22.2	22.1
9/3/13 4:00 PM	10.91	9.33	9.23	9.23	9.34	21.1	21.4	21.3	20.7	20.4
9/5/13 4:45 PM	10.90	9.30	9.25	9.23	9.31	20.3	20.6	20.4	19.8	20.0
9/6/13 11:40 AM	10.85	9.34	9.27	9.27	9.30	20.8	21.4	21.0	20.3	20.2
9/9/13 4:00 PM	10.91	9.22	9.19	9.16	9.26	21.1	20.8	20.7	20.4	20.6
9/13/13 4:15 PM	11.02	9.56	9.51	9.51	9.31	19.6	20.3	20.4	20.0	21.3
9/16/13 4:00 PM	10.89	9.59	9.55	9.53	9.29	19.5	20.4	20.5	20.1	19.9
9/18/13 4:00 PM	10.97	9.22	8.98	8.87	9.21	18.6	19.3	19.5	19.1	19.5
9/19/13 4:15 PM	10.96	9.12	9.01	8.94	9.20	19.0	19.8	19.8	19.3	20.4
9/20/13 3:20 PM	10.95	9.07	8.81	8.77	9.22	18.5	19.2	19.3	18.9	20.2
9/23/13 4:30 PM	10.96	8.95	8.96	8.90	9.27	19.4	19.0	19.1	18.6	20.3
9/25/13 5:00 PM	10.87	8.91	8.76	8.72	9.25	18.5	19.1	19.4	18.9	20.3
9/26/13 4:45 PM	11.17	8.75	8.67	8.48	9.22	18.5	19.2	19.3	19.1	20.5
9/27/13 3:15 PM	11.16	9.11	9.09	9.01	9.30	18.7	19.1	19.2	18.9	19.3
10/1/13 4:45 PM	10.87	9.13	9.10	9.07	9.27	17.9	18.6	18.7	18.5	20.0
10/2/13 4:00 PM	11.07	9.02	9.02	8.97	9.26	16.9	17.7	17.7	17.7	19.3
10/4/13 5:20 PM	11.19	9.37	9.45	9.43	9.32	15.8	16.9	16.9	16.5	18.5
10/7/13 4:00 PM	11.09	9.71	9.66	9.66	9.27	14.5	15.2	14.7	14.4	15.6
10/11/13 4:00 PM	10.92	9.78	9.73	9.72	9.27	15.0	15.5	15.4	15.2	16.3
10/14/13 11:30 AM	11.30	9.68	9.66	9.63	9.23	14.4	14.8	14.8	14.9	16.7
10/15/13 4:00 PM	11.37	9.70	9.68	9.66	9.25	13.0	13.3	13.4	13.3	16.6
10/16/13 10:00 AM	11.23	9.67	9.60	9.59	9.24	11.8	11.9	12.0	11.8	16.0
10/16/13 7:00 PM	11.23	10.52	9.78	9.73	9.24	10.8	11.0	10.9	11.1	15.1
10/18/13 5:10 PM	11.08	10.34	9.65	9.68	9.29	10.8	11.2	11.0	10.8	13.6
10/23/13 4:00 PM	11.46	11.11	9.81	9.71	9.32	9.0	9.3	9.3	9.5	12.0
10/25/13 4:00 PM	11.35	11.06	9.64	9.67	9.37	9.3	9.0	9.7	9.1	11.6
10/31/13 5:00 PM	11.51	10.93	9.83	9.68	9.27	8.1	8.2	7.9	8.2	13.7
11/1/13 3:20 PM	11.42	11.05	9.68	9.67	9.29	7.8	8.2	8.1	8.1	12.7
11/5/13 4:20 PM	11.46	10.91	9.80	9.69	9.29	7.9	7.7	7.9	7.7	12.5

Table A 2: Sample DOC and UV254

	DOC					**UV254**				
Date	**O_3 CC In.**	**S-1**	**S-2**	**S-3**	**FE**	**O_3 CC In.**	**S-1**	**S-2**	**S-3**	**FE**
mm/dd/yy	**mg/L**					**cm^{-1}**				
5/4/13 6:30 AM	2.64	2.58	2.58	2.56						
5/9/13 5:00 AM	4.67	4.47	4.33	4.32						
5/10/13 5:00 AM	4.71	4.49	4.45	4.31		0.069	0.042	0.031	0.036	
5/14/13 5:15 AM	4.97	4.83	4.68	4.60		0.072	0.043	0.037	0.029	
5/15/13 5:30 AM	5.06	4.90	4.77	4.71		0.077	0.047	0.037	0.033	
5/16/13 12:00 AM	4.85	4.76	4.61	4.53		0.075	0.037	0.032	0.026	
5/18/13 6:30 AM	5.03	4.72	4.63	4.61		0.068	0.033	0.028	0.023	
5/28/13 6:00 AM	4.49	4.43	4.24	4.15		0.063	0.032	0.025	0.026	
5/29/13 6:00 AM	4.52	4.38	4.27	4.23		0.058	0.030	0.025	0.027	
6/2/13 5:30 AM	4.29	4.17	4.03	3.98		0.051	0.029	0.024	0.021	
6/4/13 6:00 PM	4.45	4.41	4.30	4.16		0.050	0.023	0.017	0.015	
6/7/13 6:45 AM	4.34	4.08	4.01	3.95		0.048	0.023	0.019	0.017	
6/10/13 9:00 PM	4.23	4.14	3.84	3.80		0.047	0.022	0.019	0.017	
6/12/13 7:00 AM	4.02	3.94	3.64	3.76		0.043	0.022	0.019	0.017	
6/15/13 9:00 PM	3.95	3.68	3.87	3.15		0.047	0.022	0.016	0.014	
6/17/13 4:30 PM	3.78	3.88	3.66	3.48		0.046	0.021	0.018	0.016	
6/18/13 4:30 PM	2.96	3.11	2.56	2.72		0.036	0.015	0.012	0.011	
6/19/13 5:00 PM	2.77	2.54	2.52	2.37		0.035	0.018	0.012	0.011	
6/20/13 7:30 AM	2.95	2.57	2.59	2.38		0.035	0.018	0.015	0.013	
6/24/13 5:10 PM	2.17	2.46	2.06	1.89		0.036	0.023	0.016	0.015	
6/27/13 2:30 PM	2.23	2.37	2.15	2.36		0.031	0.013	0.009	0.008	
6/28/13 4:30 PM	2.44	2.21	2.11	2.06	1.58	0.035	0.014	0.010	0.009	0.010
7/1/13 8:00 PM	3.67	3.58	3.40	3.32	2.53	0.051	0.024	0.017	0.014	0.015
7/3/13 1:00 PM	3.69	3.61	3.53	3.42	2.61	0.049	0.025	0.020	0.016	0.018
7/5/13 11:45 AM	4.09	4.23	3.85	3.76	3.17	0.060	0.028	0.022	0.019	0.020
7/8/13 4:30 PM	4.31	4.19	4.02	3.97	3.39	0.056	0.026	0.020	0.017	0.018
7/10/13 5:35 PM	4.32	4.23	4.11	4.01	3.15	0.057	0.030	0.024	0.020	0.021
7/12/13 2:30 PM	4.27	4.18	4.06	3.97	3.30	0.053	0.027	0.022	0.018	0.018
7/15/13 8:45 PM	3.82	3.68	3.71	3.51	2.76	0.049	0.025	0.017	0.015	0.017
7/18/13 3:45 PM	3.28	3.19	3.12	3.10	2.48	0.037	0.022	0.016	0.014	0.013
7/19/13 3:45 PM	3.52	3.34	3.25	3.17	2.60	0.041	0.018	0.014	0.012	0.017
7/22/13 4:00 PM	3.69	3.58	3.48	3.50	2.83	0.041	0.021	0.018	0.015	0.016
7/24/13 5:30 PM	3.84	3.70	3.66	3.60	3.05	0.041	0.021	0.018	0.016	0.016
7/26/13 3:15 PM	4.03	3.90	3.75	3.74	2.98	0.041	0.022	0.016	0.014	0.014
7/29/13 4:30 PM	3.65	3.52	3.45	3.39	2.74	0.035	0.016	0.011	0.010	0.010
7/31/13 5:00 PM	4.04	4.02	3.92	3.80	3.03	0.040	0.019	0.014	0.012	0.016
8/6/13 7:00 PM	4.16	3.96	3.96	3.86	3.01	0.047	0.026	0.026	0.017	0.017
8/8/13 5:30 PM	3.89	3.83	3.71	3.62	3.03	0.040	0.020	0.015	0.013	0.014

Table A 2: Sample DOC and UV254 (continued)

	DOC					**UV254**				
Date	**O_3 CC In.**	**S-1**	**S-2**	**S-3**	**FE**	**O_3 CC In.**	**S-1**	**S-2**	**S-3**	**FE**
mm/dd/yy	**mg/L**					**cm^{-1}**				
8/9/13 3:15 PM	3.95	3.89	3.74	3.67	2.99	0.045	0.024	0.019	0.018	0.017
8/12/13 6:00 PM	3.63	3.51	3.47	3.37	2.78	0.039	0.019	0.016	0.014	0.015
8/14/13 6:10 PM	3.61	3.33	3.14	3.10	2.64	0.038	0.015	0.011	0.010	0.014
8/16/13 5:00 PM	3.53	3.43	3.32	3.26	2.57	0.037	0.022	0.016	0.014	0.013
8/19/13 5:00 PM	3.99	3.97	3.85	3.83	2.93	0.045	0.028	0.020	0.016	0.016
8/22/13 4:30 PM	3.19	2.93	2.83	2.82	2.34	0.030	0.009	0.006	0.004	0.006
8/23/13 4:20 PM	3.12	2.94	2.97	2.73	2.37	0.034	0.014	0.011	0.010	0.014
8/28/13 3:00 PM	3.04	2.73	2.69	2.51	2.17	0.031	0.012	0.008	0.007	0.010
8/30/13 3:25 PM	3.03	2.87	2.87	2.79	2.14	0.032	0.016	0.012	0.011	0.010
9/3/13 4:00 PM	3.09	2.97	3.06	2.89	2.37	0.032	0.015	0.012	0.011	0.013
9/5/13 4:45 PM	3.08	2.96	2.92	3.04	2.32	0.031	0.016	0.013	0.012	0.012
9/6/13 11:40 AM	3.34	3.31	3.26	3.28	2.49	0.031	0.014	0.012	0.013	0.011
9/9/13 4:00 PM	3.45	3.38	3.93	3.30	2.58	0.037	0.016	0.014	0.012	0.013
9/13/13 4:15 PM	3.38	3.27	3.18	3.12	2.56	0.035	0.019	0.014	0.013	0.014
9/16/13 4:00 PM	3.49	3.68	3.47	3.57	2.36	0.038	0.016	0.016	0.012	0.013
9/18/13 4:00 PM	4.79	4.59	4.52	4.39	3.47	0.063	0.033	0.024	0.021	0.033
9/19/13 4:15 PM	4.81	4.63	4.57	3.56	3.56	0.062	0.030	0.025	0.022	0.022
9/20/13 3:20 PM	4.71	4.57	4.39	4.36	3.39	0.055	0.027	0.020	0.018	0.019
9/23/13 4:30 PM	4.83	4.61	4.55	4.46	3.62	0.055	0.025	0.020	0.018	0.018
9/25/13 5:00 PM	5.44	5.02	4.87	4.88	3.91	0.064	0.032	0.025	0.023	0.022
9/26/13 4:45 PM	5.05	4.97	4.67	4.68	3.90	0.059	0.027	0.022	0.020	0.022
9/27/13 3:15 PM	4.71	4.55	4.47	4.38	3.51	0.049	0.021	0.018	0.016	0.019
10/1/13 4:45 PM	4.78	4.59	4.50	4.44	3.40	0.047	0.020	0.019	0.016	0.017
10/2/13 4:00 PM	4.82	5.08	4.58	4.49	3.55	0.051	0.025	0.023	0.020	0.020
10/4/13 5:20 PM	3.97	3.83	3.77	3.73	3.03	0.042	0.019	0.017	0.016	0.017
10/7/13 4:00 PM	4.18	4.04	3.92	3.86	3.09					
10/11/13 4:00 PM	4.41	4.40	4.32	4.24	3.56	0.046	0.023	0.019	0.017	0.020
10/14/13 11:30 AM	4.55	4.44	4.37	4.40	3.47	0.050	0.024	0.021	0.019	0.021
10/15/13 4:00 PM	3.75	3.72	3.66	3.69	3.01	0.042	0.021	0.018	0.017	0.019
10/16/13 10:00 AM	4.28	4.21	4.16	4.10	3.41	0.047	0.021	0.016	0.014	0.016
10/16/13 7:00 PM	3.37	3.29	3.23	3.21	2.50	0.043	0.023	0.017	0.015	0.017
10/18/13 5:10 PM	3.01	2.96	2.98	2.86	2.28	0.040	0.021	0.016	0.014	0.016
10/23/13 4:00 PM	3.80	3.70	3.66	3.66	3.16	0.047	0.029	0.023	0.020	0.023
10/25/13 4:00 PM	4.12	4.03	4.20	4.56	3.75	0.047	0.031	0.024	0.022	0.023
10/31/13 5:00 PM	4.17	4.09	4.06	4.06	3.59	0.049	0.031	0.025	0.023	0.025
11/1/13 3:20 PM	4.30	4.17	4.18	4.17	3.60	0.047	0.032	0.023	0.022	0.023
11/5/13 4:20 PM	4.23	4.14	4.11	4.12	3.67	0.048	0.028	0.024	0.022	0.024

Table A 3: Sample Ammonia

	Ammonia				**Ammonia**	
Date	**O_3 CC In.**	**S-1**	**S-3**	**Date**	**O_3 CC In.**	**S-3**
mm/dd/yy	**mg/L**			**mm/dd/yy**	**mg/L**	
5/4/13 6:30 AM	0.26	0.28		8/9/13 3:15 PM	0.10	0.11
5/9/13 5:00 AM	0.13	0.14		8/12/13 6:00 PM	0.09	0.09
5/10/13 5:00 AM	0.09	0.10		8/14/13 6:10 PM	0.08	0.08
5/14/13 5:15 AM	0.06	0.15		8/16/13 5:00 PM	0.09	0.10
5/15/13 5:30 AM	0.10	0.16		8/19/13 5:00 PM	0.08	0.08
5/16/13 12:00 AM	0.08	0.15		8/22/13 4:30 PM	0.19	0.19
5/18/13 6:30 AM	0.06	0.12		8/23/13 4:20 PM	0.21	0.19
5/28/13 6:00 AM	0.05	0.09		8/28/13 3:00 PM	0.18	0.16
5/29/13 6:00 AM	0.04	0.10		8/30/13 3:25 PM	0.16	0.16
6/2/13 5:30 AM	0.07	0.13		9/3/13 4:00 PM	0.15	0.14
6/4/13 6:00 PM	0.23	0.24		9/5/13 4:45 PM	0.14	0.13
6/7/13 6:45 AM	0.25	0.26		9/6/13 11:40 AM	0.11	0.11
6/10/13 9:00 PM	0.24	0.25		9/9/13 4:00 PM	0.13	0.13
6/12/13 7:00 AM	0.28	0.28		9/13/13 4:15 PM	0.12	0.12
6/15/13 9:00 PM	0.29	0.29		9/16/13 4:00 PM	0.14	0.14
6/17/13 4:30 PM	0.32	0.33		9/18/13 4:00 PM	0.13	0.13
6/18/13 4:30 PM	0.17	0.17		9/19/13 4:15 PM	0.11	0.11
6/19/13 5:00 PM	0.19	0.19		9/20/13 3:20 PM	0.11	0.13
6/20/13 7:30 AM	0.21	0.21		9/23/13 4:30 PM	0.12	0.12
6/24/13 5:10 PM	0.24	0.24		9/25/13 5:00 PM	0.15	0.17
6/27/13 2:30 PM	0.32	0.32		9/26/13 4:45 PM	0.10	0.11
6/28/13 4:30 PM	0.31	0.31	0.30	9/27/13 3:15 PM	0.10	0.10
7/1/13 8:00 PM	0.30	0.31	0.30	10/1/13 4:45 PM	0.24	0.25
7/3/13 1:00 PM	0.32	0.32	0.29	10/2/13 4:00 PM	0.24	0.25
7/5/13 11:45 AM	0.36	0.37	0.37	10/4/13 5:20 PM	0.16	0.17
7/8/13 4:30 PM	0.37	0.37	0.35	10/7/13 4:00 PM	0.13	0.13
7/10/13 5:35 PM	0.34	0.35	0.35	10/11/13 4:00 PM	0.37	0.38
7/12/13 2:30 PM	0.27	0.282	0.27	10/14/13 11:30 AM	0.41	0.40
7/15/13 8:45 PM	0.34	0.348	0.34	10/15/13 4:00 PM	0.05	0.06
7/18/13 3:45 PM	0.22	0.2	0.21	10/16/13 10:00 AM	0.04	0.05
7/19/13 3:45 PM	0.29	0.292	0.29	10/16/13 7:00 PM	0.27	0.27
7/22/13 4:00 PM	0.32	0.321	0.32	10/18/13 5:10 PM	0.21	0.22
7/24/13 5:30 PM	0.32		0.31	10/23/13 4:00 PM	0.26	0.27
7/26/13 3:15 PM	0.30		0.30	10/25/13 4:00 PM	0.24	0.24
7/29/13 4:30 PM	0.23		0.22	10/31/13 5:00 PM		
7/31/13 5:00 PM	0.12		0.12	11/1/13 3:20 PM		
8/6/13 7:00 PM	0.12		0.13	11/5/13 4:20 PM		
8/8/13 5:30 PM	0.11		0.11			

Table A 4: Ozone System Data

	CC CT			O_3 Residual			O_3 Gas Flow						Ozone
Date	**Req.**	**Act.**	**Ratio**	**S-1**	**S-2**	**S-3**	**O_3**	**S-1**	**S-2**	**S-3**	**Total**	**Gen. Total**	**Dose**
mm/dd/yy	**mgL^{-1}*min**			**ppm**			**%**	**scfm**					
5/4/13 6:30 AM	0.63	1.68	2.67	0.021	0.071	0.140	5.0	11.0	10.5	5.7	27.2		5.0
5/9/13 5:00 AM	0.58	0.85	1.47	0.042	0.071	0.042	4.1	11.7	22.8	14.0	48.5		8.0
5/10/13 5:00 AM	0.53	1.16	2.19	0.039	0.086	0.054	4.1	12.5	23.9	14.8	51.2		8.0
5/14/13 5:15 AM	0.48	0.86	1.79	0.017	0.026	0.071	4.8	10.1	25.0	14.4	49.5		8.0
5/15/13 5:30 AM	0.46	0.80	1.74	0.018	0.039	0.081	4.9	10.5	25.8	14.7	51.0		8.0
5/16/13 12:00 AM	0.43	0.87	2.02	0.022	0.031	0.095	5.0	10.9	25.0	14.6	50.5		8.0
5/18/13 6:30 AM	0.42	0.84	2.00	0.019	0.023	0.044	4.3	11.8	22.2	13.2	47.2		8.0
5/28/13 6:00 AM	0.43	0.78	1.81	0.026	0.041	0.059	4.4	14.2	23.6	14.1	51.9		8.0
5/29/13 6:00 AM	0.43	0.68	1.58	0.030	0.044	0.042	4.1	13.8	21.8	13.4	49.0		8.0
6/2/13 5:30 AM	0.41	1.15	2.80	0.033	0.064	0.081	3.9	13.6	21.6	12.5	47.6		8.0
6/4/13 6:00 PM	0.43	0.58	1.35	0.034	0.051	0.027	4.2	13.0	20.6	11.6	45.1		8.0
6/7/13 6:45 AM	0.44	0.67	1.52	0.034	0.053	0.026	4.2	14.7	22.7	12.6	49.9		8.0
6/10/13 9:00 PM	0.35	0.53	1.51	0.035	0.040	0.023	3.5	15.3	23.5	13.3	52.1		8.0
6/12/13 7:00 AM	0.34	0.69	2.03	0.034	0.054	0.048	4.3	14.6	22.0	12.8	49.5		8.0
6/15/13 9:00 PM	0.28	0.61	2.18	0.023	0.053	0.036	4.4	15.7	22.0	13.5	51.2		8.0
6/17/13 4:30 PM	0.25	0.63	2.52	0.030	0.040	0.061	4.8	16.2	21.7	14.2	52.1		8.0
6/18/13 4:30 PM	0.32	0.93	2.91	0.041	0.068	0.096	5.0	15.8	21.1	13.7	50.6		7.8
6/19/13 5:00 PM	0.31	0.58	1.87	0.040	0.047	0.051	5.0	15.6	20.1	13.0	48.7		7.8
6/20/13 7:30 AM	0.31	0.62	2.00	0.041	0.050	0.048	4.9	15.6	20.0	13.8	49.4		7.8
6/24/13 5:10 PM	0.37	0.76	2.05	0.043	0.046	0.043	4.2	8.7	10.1	7.6	26.4		4.0
6/27/13 2:30 PM	0.35	0.81	2.31	0.038	0.040	0.055	5.2	7.9	11.0	6.3	25.2		5.2
6/28/13 4:30 PM	0.31	0.45	1.45	0.038	0.039	0.025	3.5	13.7	25.0	12.7	51.4		6.6
7/1/13 8:00 PM	0.27	0.39	1.44	0.019	0.020	0.037	4.4	12.9	23.6	12.3	48.7		7.0
7/3/13 1:00 PM	0.27		0.00	0.003	0.082	0.085	4.6	13.1	25.4	13.3	51.8		7.0
7/5/13 11:45 AM	0.25	0.85	3.40	0.007	0.038	0.079	4.6	13.2	18.0	13.2	44.4		6.8
7/8/13 4:30 PM	0.25	0.64	2.56	0.001	0.020	0.102	4.2	12.2	22.1	11.9	46.3		6.8
7/10/13 5:35 PM	0.26	0.42	1.62	0.002	0.010	0.052	4.0	13.7	23.7	13.1	50.4		6.4
7/12/13 2:30 PM	0.25	0.53	2.12	0.008	0.050	0.039	4.8	13.4	24.1	13.2	50.7		7.3
7/15/13 8:45 PM	0.31	0.86	2.77	0.005	0.050	0.063	5.7	9.2	11.5	7.6	28.3		6.2
7/18/13 3:45 PM	0.26	1.41	5.42	0.068	0.074	0.024	4.0	5.8	9.8	5.8	21.4		4.7
7/19/13 3:45 PM	0.26	1.28	4.92	0.042	0.091	0.031	4.0	3.1	11.3	7.4	21.9		5.4
7/22/13 4:00 PM	0.32	1.03	3.22	0.012	0.112	0.061	3.5	12.7	17.2	16.8	46.7	55.0	5.6
7/24/13 5:30 PM	0.31	0.98	3.16	0.045	0.116	0.063	3.3	14.2	19.5	19.4	53.1	63.1	5.2
7/26/13 3:15 PM	0.29	0.71	2.45	0.005	0.088	0.038	3.9	14.0	16.4	17.6	48.0	55.2	6.0
7/29/13 4:30 PM	0.31	0.80	2.58	0.011	0.088	0.054	3.7	14.6	16.9	18.4	49.8	58.7	5.5
7/31/13 5:00 PM	0.30	0.60	2.00	0.011	0.062	0.046	4.1	14.5	16.3	18.2	49.0	57.3	6.0
8/6/13 7:00 PM	0.32	0.88	2.75	0.007	0.069	0.063	3.9	9.7	20.4	18.8	48.9	56.5	6.2
8/8/13 5:30 PM	0.32	0.77	2.41	0.014	0.051	0.075	3.6	9.9	21.2	19.6	50.7	59.1	5.8

Table A 4: Ozone System Data (continued)

	CC CT			O_3 Residual			O_3 Gas Flow						Ozone
Date	**Req.**	**Act.**	**Ratio**	**S-1**	**S-2**	**S-3**	**O_3**	**S-1**	**S-2**	**S-3**	**Total**	**Gen. Total**	**Dose**
mm/dd/yy	**mgL^{-1}*min**			**ppm**			**%**	**scfm**					
8/9/13 3:15 PM	0.33	0.81	2.45	0.008	0.071	0.063	3.6	10.0	20.6	19.2	49.7	60.7	5.8
8/12/13 6:00 PM	0.30	0.67	2.23	0.028	0.053	0.062	4.0	10.1	20.3	19.7	50.2	60.9	6.0
8/14/13 6:10 PM	0.28	0.72	2.57	0.010	0.095	0.002	4.8	5.8	4.9	9.8	20.5	54.0	5.7
8/16/13 5:00 PM	0.29	0.62	2.14	0.016	0.020	0.039	4.6	5.9	12.4	11.4	29.6	60.8	6.7
8/19/13 5:00 PM	0.24	0.60	2.50	0.013	0.017	0.046	5.5	5.3	12.1	10.9	28.3	58.0	7.5
8/22/13 4:30 PM	0.26	0.75	2.88	0.007	0.094	0.008	4.6	6.5	8.9	10.9	26.3	57.1	5.4
8/23/13 4:20 PM	0.27	0.75	2.78	0.014	0.094	0.017	4.5	6.1	7.6	9.6	23.3	53.9	5.2
8/28/13 3:00 PM	0.26	0.67	2.58	0.012	0.064	0.026	4.9	7.1	9.4	11.7	28.3	65.0	6.0
8/30/13 3:25 PM	0.27	0.70	2.59	0.028	0.037	0.027	4.7	10.8	6.4	5.5	22.7	54.1	5.6
9/3/13 4:00 PM	0.31	0.62	2.00	0.012	0.047	0.022	4.2	10.9	8.3	5.8	25.0	56.5	5.0
9/5/13 4:45 PM	0.35	1.12	3.20	0.028	0.087	0.036	3.8	10.0	7.8	5.5	23.3	52.9	4.4
9/6/13 11:40 AM	0.32	0.54	1.69	0.009	0.037	0.032	4.3	11.4	9.3	6.2	26.9	61.2	4.9
9/9/13 4:00 PM	0.31	2.45	7.90	0.183	0.155	0.050	3.3	14.4	22.0	8.3	44.8	52.6	5.3
9/13/13 4:15 PM	0.33	0.75	2.27	0.055	0.042	0.018	5.9	9.5	12.1	5.7	27.2	31.4	5.0
9/16/13 4:00 PM	0.33	0.44	1.33	0.042	0.053	0.021	7.4	10.4	12.5	6.0	28.9	33.1	7.8
9/18/13 4:00 PM	0.37	1.93	5.22	0.039	0.106	0.153	6.5	10.8	13.6	5.3	29.7	34.6	7.0
9/19/13 4:15 PM	0.35	0.38	1.09	0.014	0.018	0.031	6.6	9.5	11.1	4.7	25.2	29.9	6.3
9/20/13 3:20 PM	0.36	1.04	2.89	0.024	0.036	0.081	5.8	10.5	12.4	5.0	27.9	31.5	6.6
9/23/13 4:30 PM	0.38	1.50	3.95	0.046	0.095	0.144	6.5	10.8	12.6	5.2	28.6	32.4	6.2
9/25/13 5:00 PM	0.37	0.71	1.92	0.035	0.043	0.063	4.5	15.8	22.1	7.2	45.0	53.1	7.0
9/26/13 4:45 PM	0.37	2.05	5.54	0.099	0.126	0.139	3.4	16.4	23.3	7.7	47.3	56.1	6.4
9/27/13 3:15 PM	0.37	0.93	2.51	0.059	0.074	0.052	3.2	16.5	22.6	7.6	46.8	55.3	6.0
10/1/13 4:45 PM	0.39	0.56	1.44	0.054	0.059	0.005	3.2	14.2	17.6	6.5	38.3	44.9	6.2
10/2/13 4:00 PM	0.41	1.21	2.95	0.092	0.081	0.060	5.6	10.3	10.9	5.0	26.1	30.0	5.9
10/4/13 5:20 PM	0.46	1.08	2.35	0.089	0.114	0.045	5.4	10.4	10.4	4.9	25.6	27.9	5.2
10/7/13 4:00 PM	0.51	0.94	1.84	0.060	0.090	0.030	5.5	10.1	11.0	4.7	25.7		5.6
10/11/13 4:00 PM	0.49	0.76	1.55	0.039	0.099	0.046	6.8	9.6	11.3	4.6	25.4	28.7	5.4
10/14/13 11:30 AM	0.51	1.14	2.24	0.094	0.095	0.044	6.2	9.2	11.6	4.6	25.4	28.8	6.1
10/15/13 4:00 PM	0.58	1.43	2.47	0.044	0.112	0.078	4.3	9.7	11.2	4.7	25.5	28.9	4.3
10/16/13 10:00 AM	0.63	0.98	1.56	0.046	0.063	0.062	4.8	10.4	11.8	4.7	26.9	30.5	5.0
10/16/13 7:00 PM	0.64	1.61	2.52	0.008	0.059	0.113	4.2	8.7	11.2	5.6	25.5	28.4	4.6
10/18/13 5:10 PM	0.64	0.90	1.41	0.007	0.041	0.066	3.5	9.6	11.1	5.4	26.1	29.9	3.6
10/23/13 4:00 PM	0.70	1.24	1.77	0.011	0.070	0.112	3.8	12.0	8.3	3.9	24.2	26.0	3.0
10/25/13 4:00 PM	0.71	1.23	1.73	0.014	0.078	0.084	3.1	12.2	8.7	3.8	24.7	27.2	2.9
10/31/13 5:00 PM	0.74	1.07	1.45	0.011	0.072	0.051	3.2	15.4	7.4	2.8	25.6	28.1	3.6
11/1/13 3:20 PM	0.75	1.03	1.37	0.012	0.064	0.053	3.3	15.2	9.0	3.0	27.1	30.1	3.9
11/5/13 4:20 PM	0.74	1.43	1.93	0.009	0.097	0.094	4.0	15.5	7.7	3.0	26.2	28.7	3.8

Table A 5: Bromate and Bromide Sample Data

	Bromate				**Bromide**	
Date	**S-1**	**S-2**	**S-3**	**Reservoir**	**O_3 CC In.**	**S-3**
mm/dd/yy	**ppb**				**ppm**	
5/4/13 6:30 AM	0.47	0.31	1.29	0.00	0.03	0.03
5/9/13 5:00 AM	0.00	2.19	3.18	0.00	0.02	0.05
5/10/13 5:00 AM	0.00	2.01	3.25	0.00	0.05	0.04
5/14/13 5:15 AM	0.46	3.40	4.65	4.65	0.03	0.04
5/15/13 5:30 AM	0.64	2.23	5.46	0.00	0.03	0.04
5/16/13 12:00 AM	0.83	3.86	4.62	5.90	0.04	0.04
5/18/13 6:30 AM	0.98	3.66	3.69	4.73	0.05	0.05
5/28/13 6:00 AM	1.88	7.82	11.92	8.43	0.03	0.05
5/29/13 6:00 AM	3.29	8.28	11.12	11.23	0.06	0.03
6/2/13 5:30 AM	4.51	9.06	15.51	10.70	0.05	0.05
6/4/13 6:00 PM	1.26	4.06	7.41	6.40	0.08	0.07
6/7/13 6:45 AM	1.92	5.79	7.50	7.95	0.05	0.08
6/10/13 9:00 PM	1.80	5.48	7.52	8.38	0.07	0.07
6/12/13 7:00 AM	3.46	5.64	8.85	8.47	0.07	0.06
6/15/13 9:00 PM	2.29	7.30	8.68	7.32	0.04	0.06
6/17/13 4:30 PM	1.90	5.53	7.38	6.92	0.06	0.07
6/18/13 4:30 PM	2.06	3.47	4.95	1.31	0.06	0.06
6/19/13 5:00 PM	2.18	3.64	5.20	3.68	0.07	0.05
6/20/13 7:30 AM	1.53	2.96	4.13	3.72	0.06	0.06
6/24/13 5:10 PM	0.33	0.56	1.07	1.32	0.05	0.03
6/27/13 2:30 PM	0.64	1.80	2.97	1.17	0.05	0.04
6/28/13 4:30 PM	0.70	1.69	1.94	1.48	0.05	0.04
7/1/13 8:00 PM	0.47	0.52	0.88	0.99	0.06	0.06
7/3/13 1:00 PM	0.43	0.99	1.48	1.18	0.05	0.06
7/5/13 11:45 AM	0.35	0.70	1.16	1.11	0.07	0.08
7/8/13 4:30 PM	0.53	0.47	0.67	0.72	0.07	0.08
7/10/13 5:35 PM	0.57	0.57	0.64	0.74	0.09	0.08
7/12/13 2:30 PM	0.16	0.43	0.54	0.00	0.09	0.09
7/15/13 8:45 PM	0.00	0.00	0.52	0.39	0.06	0.06
7/18/13 3:45 PM	0.17	0.17	0.24	0.00	0.07	0.07
7/19/13 3:45 PM	0.36	0.65	0.64	0.28	0.08	0.07
7/22/13 4:00 PM	0.30	0.30	0.00	0.26	0.08	0.06
7/24/13 5:30 PM	0.20	0.20	0.49	0.36	0.06	0.07
7/26/13 3:15 PM	0.56	1.83	2.60	3.80	0.07	0.07
7/29/13 4:30 PM	1.51	3.51	3.88	2.00	0.06	0.06
7/31/13 5:00 PM	1.75	4.49	5.86	6.77	0.06	0.08
8/6/13 7:00 PM	0.72	2.16	4.00	4.73	0.06	0.06
8/8/13 5:30 PM	0.95	2.73	6.02	3.73	0.06	0.07

Table A 5: Bromate and Bromide Sample Data (continued)

	Bromate				**Bromide**	
Date	**S-1**	**S-2**	**S-3**	**Reservoir**	**O_3 CC In.**	**S-3**
mm/dd/yy	**ppb**				**ppm**	
8/9/13 3:15 PM	0.73	2.38	4.74	4.63	0.05	0.06
8/12/13 6:00 PM	1.67	4.43	7.33	4.48	0.06	0.05
8/14/13 6:10 PM	4.72	11.40	13.50	5.88	0.04	0.05
8/16/13 5:00 PM	0.94	2.50	4.08	6.21	0.05	0.06
8/19/13 5:00 PM	0.96	2.06	5.55	6.17	0.07	0.07
8/22/13 4:30 PM	6.53	15.26	17.10	0.95	0.05	0.06
8/23/13 4:20 PM	0.77	13.39	15.26	6.64	0.06	0.05
8/28/13 3:00 PM	8.95	14.79	17.86	5.59	0.06	0.05
8/30/13 3:25 PM	3.42	5.10	6.79	0.73	0.06	0.06
9/3/13 4:00 PM	0.00	0.50	5.61	4.55	0.06	0.07
9/5/13 4:45 PM	0.59	2.79	5.88	5.19	0.05	0.06
9/6/13 11:40 AM	2.87	0.51	6.22	0.00	0.06	0.06
9/9/13 4:00 PM	1.57	0.54	1.01	7.36	0.06	0.05
9/13/13 4:15 PM	1.81	0.58	0.88	5.60	0.06	0.06
9/16/13 4:00 PM	2.68	4.55	9.51	5.45	0.04	0.04
9/18/13 4:00 PM	0.38	3.10	2.43	2.49	0.06	0.06
9/19/13 4:15 PM	1.00	1.41	0.90	2.12	0.06	0.05
9/20/13 3:20 PM	0.92	1.64	1.71	1.81	0.06	0.06
9/23/13 4:30 PM	0.63	0.63	1.58	0.66	0.07	0.07
9/25/13 5:00 PM	0.93	1.11	0.40	0.39	0.06	0.07
9/26/13 4:45 PM	0.32	0.32	4.47	0.58	0.07	0.07
9/27/13 3:15 PM	1.04	1.19	1.02	0.91	0.06	0.07
10/1/13 4:45 PM	0.63	1.48	1.15	1.23	0.07	0.07
10/2/13 4:00 PM	0.59	1.35	1.39	0.95	0.06	0.07
10/4/13 5:20 PM	2.37	4.30	5.89	3.34	0.05	0.05
10/7/13 4:00 PM	1.62	3.68	5.11	6.06	0.05	0.05
10/11/13 4:00 PM	0.97	1.90	2.40	3.11	0.05	0.05
10/14/13 11:30 AM	1.30	1.60	2.22	2.26	0.06	0.06
10/15/13 4:00 PM	3.14	4.28	5.66	3.74	0.05	0.05
10/16/13 10:00 AM	1.97	3.35	7.65	4.02	0.05	0.05
10/16/13 7:00 PM	1.79	3.53	4.62	3.44	0.08	0.08
10/18/13 5:10 PM	0.52	0.65	1.37	2.77	0.05	0.05
10/23/13 4:00 PM	0.24	1.39	0.57	0.62	0.08	0.09
10/25/13 4:00 PM	0.04	0.39	0.92	0.04	0.09	0.09
10/31/13 5:00 PM	0.26	0.63	0.98	0.00	0.12	0.13
11/1/13 3:20 PM	0.00	0.82	0.83	0.05	0.12	0.12
11/5/13 4:20 PM	0.61	0.26	1.04	0.79	0.11	0.12