AN INVESTIGATION INTO BROMATE FORMATION IN OZONE DISINFECTION SYSTEMS

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MASTER OF SCIENCE

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ABSTRACT

Ozonation is used as an alternative disinfection process to chlorination but unfortunately has a potential of oxidizing bromide, a natural component of water sources, to bromate. Bromate is a possible carcinogen with a maximum contaminant level of 10 ppb. To understand bromate formation in full-scale systems, a comprehensive study was conducted at the Moorhead Water Treatment Plant (WTP). Bromide concentrations in source waters were monitored. Water samples from locations in the ozonation chambers were collected and analyzed for bromate and other parameters. Results showed that bromate formation was increased through increases in pH, bromide, and ozone dose during high temperatures and was decreased by increases in organics. The impact of the bromate influential parameters was minimized at low temperatures. To assist Moorhead WTP on developing bromate control strategies, a modeling approach was adopted to predict bromate formation at various operational conditions using temperature, pH, ozone dose, bromide, and TOC.

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DEDICATION

In dedication with all my love to my nephew Briggs Terrence and my niece Alivia Lee:

keep your dreams in sight, reach for the stars, and never stop learning!

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AWWA	American Water Works Association
Br^-	bromide
$BrO\bullet$	bromine oxide radical
$Br\bullet$	bromine radical
BrO_2^-	bromite
BrO_3^-	bromate
CO_2	carbon dioxide
CT	contact time
DBP	disinfection byproduct
DOC	dissolved organic carbon
ft	feet
gpm	gallons per minute
$^\bullet OH$	hydroxyl radical
OBr^-	hypobromite
HOBr	hypobromous acid
IARC	International Agency for the Research on Cancer
IC	ion chromatography
MCL	maximum contaminant level
mg/L	milligrams per liter
MGD	million gallons per day
MDH	Minnesota Department of Health

NOM	natural organic matter
O_3	ozone
ppb	parts per billion
ppm	parts per million
ft^2	square feet
SCADA	Supervisory Control and Data Acquisition
TOC	total organic carbon
USEPA	United States Environmental Protection Agency
WTP	water treatment plant

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CHAPTER 1. INTRODUCTION

For many years the primary additive used to disinfect drinking water has been chlorine. Recently, however, the use of ozone as a disinfection agent has become popular. Ozone is highly reactive and may form hydroxyl radicals under alkaline conditions, making it one of the strongest oxidants and disinfectants of the oxygen species (Hoigne and Bader, 1976). Due to ozone's high oxidation potential it has the ability to not only disinfect drinking water but also remove inorganic and natural organic substances making it an option for disinfection as well as taste and odor control (Staehelin et al., 1984). The use of ozone also reduces the formation of trihalomethanes and other chlorine disinfection byproducts (DBPs) that often stem from the use of chlorine in disinfection (Glaze et al., 1982; Camel and Bermond, 1998). Although ozone has removed many of the dangers associated with the disinfection process it does bring about its own concerns. Ozone has the potential of oxidizing bromide, found naturally in many source waters, to bromate (Haag and Hoigne, 1983).

In the early 1990's, the International Agency for the Research on Cancer (IARC) classified bromate as a possible carcinogen (IARC, 1999). As part of the United States Environmental Protection Agency (USEPA) Stage 1 Disinfectants/Disinfection Byproducts Rule a maximum contaminant level (MCL) for bromate was set to 10 ppb for water treatment plants utilizing ozone (USEPA, 1998). Unfortunately, knowledge on bromate formation is limited and many municipalities do not have the capability to test for bromate. To understand the operation of a treatment plant for minimization of bromate, a greater understanding of bromate formation in full-scale water treatment processes is needed. Bench and pilot scale size research efforts do not provide for operational changes that are applied to full-scale systems. In addition, it is very difficult to mimic the exact disinfection process that occurs in full-scale in a small scale system.

Changes in the application of ozone, contact time, and operational differences provide margins of error in a bench or pilot sized system. Once a connection is made between bromate formation and water quality characteristics on a full-scale system, water treatment plant operators would have the ability to estimate the amount of bromate that may form in the resulting drinking water and alter their operating conditions to reduce the formation. The formation of bromate is a common concern that may occur at all water treatment plants that use ozone as a disinfection agent. In particular, it is a major concern for the Moorhead Water Treatment Plant (WTP) in Moorhead, MN. During the summer months, ozone demand increases with the increase in temperature, total organic carbon (TOC), and flow rate through the disinfection chambers. In order to meet proper disinfection contact times, the Moorhead WTP increases the ozone dose and in effect is possibly providing the opportunity for more bromate to form. Knowledge on bromate formation in a full-scale system is needed to ensure safe drinking water standards are met and to assist municipalities, such as Moorhead, in better understanding their bromate formation. With the improved understanding, municipalities may be able to remain in compliance through more efficient water plant operation and control.

1.1. Goal and Objectives of Research

The overall goal of this project is to quantify the bromate formation in the disinfection process and identify operational strategies to minimize bromate formation. The objectives outlined to meet the research goal of this project include the following:

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

1.2. Scope of Work

To achieve the goal and objectives of the research project, individual tasks were developed. These tasks were designed and refined as more knowledge was obtained during the research project. The project was divided into four tasks: literature review, historical data analysis, water sampling and analyses, and bromate formation model development.

1.2.1. Task 1: Literature Review

Task 1 was constructed to develop a current state of understanding of the knowledge available on bromate formation during the water disinfection process. The literature spanned approximately 30 years of research. In addition, documents such as the design manual and operating manuals were reviewed for the Moorhead WTP facility. The information gained from the reviews was then used to produce tasks 2-4.

1.2.2. Task 2: Historical Data Analysis

A historical analysis was conducted for the Moorhead WTP that specifically considered data that was found to be influential to bromate formation through the literature review in task 1. The historical data analysis was developed to determine long term changes in the general water quality characteristics over a 10 year period. The historical analysis provided insight into parameters such as TOC and temperature as well as changes in treatment techniques at the Moorhead WTP. Throughout the historical analysis a more in-depth analysis was considered for the 2011 year of data to better understand seasonal changes in source water selection based on water demand, temperature, and TOC. Through the knowledge achieved with the historical data analysis, sampling requirements were improved and an overall understanding of the plant's operation was discovered.

1.2.3. Task 3: Water Sampling and Analyses

Water sampling was completed for the collection of bromide and bromate concentrations. The samples were also analyzed for those water quality parameters found to be influential to bromate formation through task 1. Sample locations were selected based on the knowledge gained from task 2 through the historical analysis of the Moorhead WTP. Operational data, water quality data, and bromide concentrations were compared to the bromate formation to determine qualitative relationships.

1.2.4. Task 4: Bromate Formation Model Development

The qualitative relationships determined in task 1 and verified in task 3 were then used to develop a bromate prediction model. Through the use of the model, a more quantitative relationship between bromate and water quality parameters was made. The model will be of assistance to operators and staff at the Moorhead WTP to help them to optimize operational settings to reduce bromate formation. A regression based model was chosen for implementation. The model was refined to improve on simplicity, ease of implementation to the Supervisory Control and Data Acquisition (SCADA) system, and ability to be controlled by operators. A predictive model that can be easily adopted by the Moorhead WTP was developed.

CHAPTER 2. BACKGROUND

Historically, research on the formation of bromate through the use of ozone in water disinfection began through an analysis of the chemistry that occurs during the oxidation of the bromide ion to bromate. As a greater understanding of bromate formation chemistry was achieved, influential factors involving the chemistry process were discovered. pH, ammonia, ozone dose, organics, temperature, and bromide were discovered as influential parameters on bromate formation. As these parameters were determined, the focus of bromate research moved to minimization techniques and operational considerations. This literature review spanned about 30 years.

2.1. Chemistry of Bromate Formation in Ozonation Process

In water treatment, bromate is formed through the oxidation of the bromide ion to bromate by ozone (O_3) or hydroxyl radicals ($^{\bullet}OH$) in the ozone disinfection process. This oxidation process, however, can be very complex and can be influenced by different water quality parameters depending on source water quality and operational conditions. The process of bromate formation is also unique as hydroxyl radicals form through the decomposition of ozone and can influence bromate formation chemistry because they are the strongest oxidants in water (Staehelin and Hoigne, 1985). The oxidation states of the important oxidants in bromate formation along with the controlling oxidizing species in each formation are described in Table 1. Through Table 1 it can be seen that each bromine species is oxidized by either O_3 alone, $^{\bullet}OH$ alone, or through the combination of O_3 and $^{\bullet}OH$ (von Gunten, 2003).

Table 1: Bromine species formed during the bromate oxidation process (von Gunten, 2003)

Species	Chemical formula	Bromine oxidation state	Controlling Oxidizing Species
Bromide	Br^-	-I	O_3, $^{\bullet}OH$
Bromine radical	$Br^{\bullet}$	0	O_3
Hypobromous acid	HOBr	+I	$^{\bullet}OH$
Hypobromite	OBr^-	+I	O_3, $^{\bullet}OH$, $CO_3^{\bullet -}$
Bromine oxide radical	$BrO^{\bullet}$	+II	---
Bromite	BrO_2^-	+III	O_3
Bromate	BrO_3^-	+V	---

Bromate formation pathways can be condensed into three processes: direct oxidation, direct/indirect oxidation, and indirect/direction oxidation, as shown in Figure 1. During the process of direct oxidation, the bromide ion is converted to bromate through the addition of molecular ozone (Figure 1, Equation 1). The reaction proceeds stepwise starting with the bromide ion oxidized to hypobromite, followed by bromite, and finally bromate (Pinkernell and von Gunten, 2001; von Gunten, 2003).

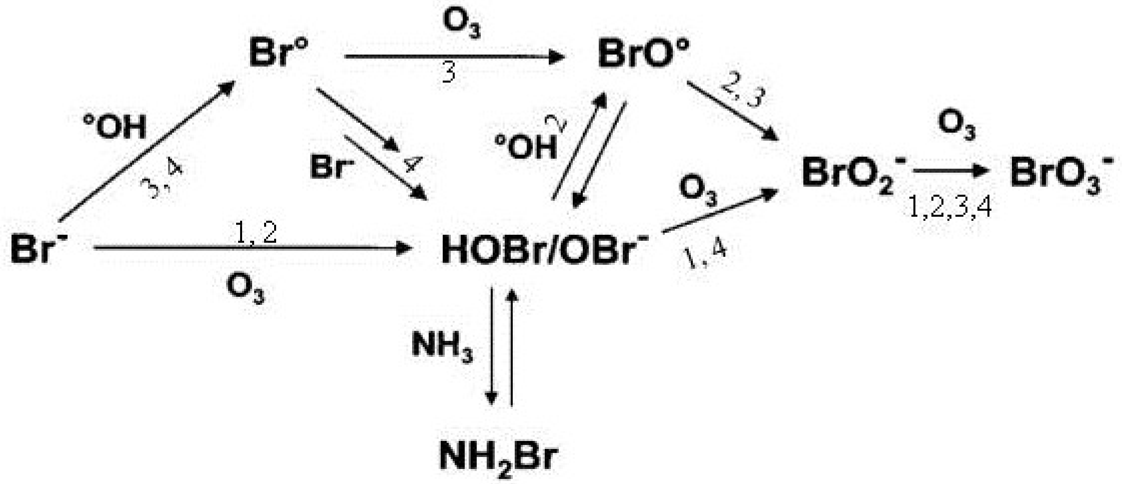

Figure 1: Bromate formation pathways (adapted from Pinkernell and von Gunten, 2001)

$$\text{Direct Oxidation: } Br^- \xrightarrow{O_3} OBr^- \xrightarrow{O_3} BrO_2^- \xrightarrow{O_3} BrO_3^- \quad (1)$$

$$\text{Direct/Indirect Oxidation: } Br^- \xrightarrow{O_3} HOBr/OBr^- \xrightarrow{^{\bullet}OH} BrO^{\bullet} \longrightarrow BrO_2^- \xrightarrow{O_3} BrO_3^- \quad (2)$$

$$\text{Indirect/Direct Oxidation: } Br^- \xrightarrow{^{\bullet}OH} Br^{\bullet} \xrightarrow{O_3} BrO^{\bullet} \longrightarrow BrO_2^- \xrightarrow{O_3} BrO_3^- \quad (3)$$

$$\text{Indirect/Direct Oxidation: } Br^- \xrightarrow{^{\bullet}OH} Br^{\bullet} \xrightarrow{Br^-} OBr^- \xrightarrow{O_3} BrO_2^- \xrightarrow{O_3} BrO_3^- \quad (4)$$

Through the direct/indirect pathway, bromate is formed through oxidation by O_3 followed by oxidation by $^{\bullet}OH$ (Figure 1, Equation 2). In this pathway, bromide ion is first oxidized by O_3 to form hypobromite (OBr^-) and is then oxidized by $^{\bullet}OH$ to the bromine oxide radical ($BrO^{\bullet}$). The bromine oxide radical then disproportionates to bromite (BrO_2^-) and then through direct oxidation produces bromate (Song et al., 1996b; Song et al., 1997; Pinkernell and von Gunten, 2001).

The third formation pathway for bromate formation, the indirect/direct pathway, occurs through indirect oxidation followed by direct oxidation. Through indirect oxidation by $^{\bullet}OH$, the bromide ion itself is oxidized by the $^{\bullet}OH$ to the bromide species, the bromine radical ($Br^{\bullet}$). At this point in the pathway, the bromine radical can either be further oxidized by O_3 to form the bromine oxide radical (Figure 1, Equation 3) or can follow a different path through the combination of bromide ions to return to the hypobromous acid/hypobromite state (Figure 1, Equation 4). Either pathway then proceeds to the formation of bromite and then bromate through direct oxidation (Song et al., 1996b; Song et al., 1997; Pinkernell and von Gunten, 2001).

The exact pathway that is followed during the ozone disinfection process is dependent on other quality characteristics of the water (Elovitz et al., 2000). Overall, however, the oxidation process is faster, but less efficient through hydroxyl radical oxidation than the oxidation through molecular ozone (Pinkernell and von Gunten, 2001).

2.2. Influential Factors on the Formation of Bromate

It is important to consider the different bromate formation pathways as they provide insight into different water quality components that may lead to increased bromate formation. For example, changes in pH, ammonia, ozone dose, organics, temperature, and bromide concentration can all influence bromide oxidation down a certain bromate formation pathway or simply lead to more or less formation. As bromate formation became a concern in the drinking water field, bromate research began to determine those factors in water quality that influence its formation. Through many different research projects a relationship between bromate formation and the following water quality characteristics have thus far been determined: pH, ammonia addition, ozone dose, organics, temperature, and bromide concentration.

2.2.1. Influence of pH on Bromate Formation

The reaction of HOBr to OBr^-, as shown in Figure 1, is pH dependent. The hypobromous acid (HOBr) only reacts further with ozone when it is in its ionized form, hypobromite (OBr^-). The concentration of HOBr is greater at low pH values and $HOBr/OBr^-$ decreases as the pH increases. Understanding that bromate requires the oxidation of OBr^- provides the idea that bromate formation increases at higher pH values (Haag and Hoigne, 1983; Siddiqui and Amy, 1993; von Gunten and Hoigne, 1994; Pinkernell and von Gunten, 2001). As shown in Figure 2, at low pH (high H^+ concentration), HOBr reacts with dissolved organic matter to form brominated organic compounds resulting in a decreased bromate formation (von Gunten and Hoigne, 1994). In addition, at higher pH values, the production of $^{\bullet}OH$ is increased promoting the hydroxyl radical pathways which have been found to be faster pathways for bromate formation (von Gunten and Hoigne, 1994; Pinkernell and von Gunten, 2001; Legube et al., 2004).

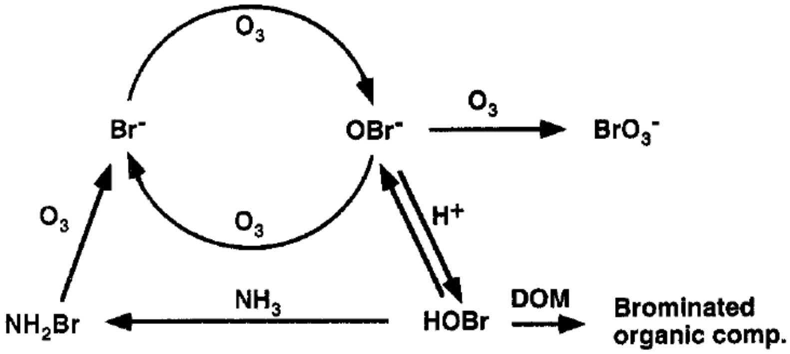

Figure 2: Bromate formation reductions during direct oxidation (von Gunten and Hoigne, 1994)

2.2.2. Influence of Ammonia Addition on Bromate Formation

Also displayed in Figure 2 is the addition of ammonia and its role in bromate formation pathways. With the addition of ammonia, bromate formation is reduced as ammonia tends to react with HOBr/OBr$^-$ to form monobromamine which is slowly oxidized by ozone back to bromide (von Gunten and Hoigne, 1994). Unfortunately, as shown in Figure 2, ammonia addition only has an effect on the HOBr/OBr$^-$ stage in bromate formation. The lack of effect on other stages allows for an uninterrupted initial oxidation of bromide through $^{\bullet}$OH and possibly bromate formation through indirect/direct oxidation pathways (Song et al., 1997; Pinkernell and von Gunten, 2001). In a study by Pinkernell and von Gunten (2001) it was determined that ammonia addition is only influential up to a certain concentration of ammonia. In their study, a maximum application of ammonia of 200 µg/L was used with no further benefit found with higher concentrations applied.

2.2.3. Influence of Ozone Dose on Bromate Formation

Increases in ozone dose correlate to increases in bromate formation due to the increase in concentration available to oxidize (Shukairy et al., 1994; Galey et al., 2004; Legube et al., 2004). Changes in ozone dose have an effect on the bromate formation rate and can affect other bromate influential parameters. The different bromate formation pathways discussed in Figure 1 occur at different rates. Table 2 contains the reaction rates of the direct oxidation of bromide to bromate. As shown in the Table 2, O_3 oxidation of the OBr^- is much faster than HOBr. Also, once the bromate formation pathway reaches BrO_2^- bromate forms very quickly as a result of the presence of O_3 (Haag and Hoigne, 1983; von Gunten and Hoigne, 1994). However, at low ozone doses, ozone can be easily consumed by other ozone demanding constituents in water such as natural organic matter (NOM) leaving bromide unoxidized. In a study conducted by Galey and colleagues, both a batch and pilot scale study were conducted to determine the impact of ozone dose, pH, temperature, and contact time of bromate formation. The authors determined ozone dose and a cross-effect between ozone dose and pH to be the most influential parameters on bromate formation. At low ozone doses, the influence of other parameters was diminished in both the batch and pilot scale experiments (Galey et al., 2004).

Table 2: Molecular ozone reaction rates (adapted from von Gunten and Hoigne, 1994)

No.	Reaction	k ($M^{-1}s^{-1}$) or pK_a (20°C)
1	$O_3 + Br^- \rightarrow O_2 + OBr^-$	160
2	$O_3 + OBr^- \rightarrow 2O_2 + Br^-$	330
3a	$O_3 + OBr^- \rightarrow BrO_2^- + O_2$	100
3b	$O_3 + HOBr \rightarrow BrO_2^- + O_2 + H^+$	≤ 0.013
4	$BrO_2^- + O_3 \rightarrow BrO_3^-$	$>10^5$
5	$HOBr \leftrightarrow H^+ + OBr^-$	9 (8.8)
6	$HOBr + NH_3 \rightarrow NH_2Br + H_20$	8×10^7
7	$O_3 + NH_2Br \rightarrow Y^\alpha$	40
8	$Y + 2O_3 \rightarrow 2H^+ NO_3^- + Br^- + 3O_2$	$k_8 >> k_7$
9	$NH_4^+ \leftrightarrow H^+ + NH_3$	9.3

$^\alpha$Y are unknown products that react in later reactions.

At high ozone doses, and high pH, hydroxyl radicals may form leading to different reaction rates and pathways to bromate formation. Table 3 contains the reaction rates of the hydroxyl radical oxidation of the bromine species. Comparing the reaction rates between molecular ozone and hydroxyl radicals, hydroxyl radical reactions rates are faster.

Table 3: Hydroxyl radical reaction rates (adapted from von Gunten and Hoigne, 1994)

No.	Reaction	k ($M^{-1}s^{-1}$) or pK_a (20°C)
10	$Br^- + OH \leftrightarrow BrOH^-$	10^{10}; 3.3×10^7
11	$BrOH^- \rightarrow Br + OH^-$	4.2×10^6
12	$Br + Br^- \rightarrow Br_2^-$	10^{10}
13	$Br_2^- + Br_2^- \rightarrow Br_3^- + 2Br^-$	2×10^9
14	$Br_2^- + OBr^- \rightarrow BrO + 2Br^-$	8×10^7
15	$OH + OBr^- \rightarrow BrO + OH^-$	4.5×10^9
16	$OH + HOBr \rightarrow BrO + H_2O$	2×10^9
17	$2BrO + H_2O \rightarrow BrO^- + BrO_2^- + 2H^+$	4.9×10^9

2.2.4. Influence of Organics on Bromate Formation

The interaction between ozone, organics, and bromate formation is complex and has produced different hypotheses between researchers. In general, research seems to be split between two ideas. First, it has been suggested that increases in organic matter tend to decrease bromate formation (Siddiqui and Amy, 1993; Song et al., 1996b; Westerhoff et al., 1998). Organic matter has been found to be a scavenger of hydroxyl radicals, slowing or preventing the bromate formation pathway from continuing through to final oxidation. In a study by Song et al. (1996b), ozone dose was kept constant and dissolved organic carbon (DOC) levels increased to find a decrease in bromate formation. Westerhoff et al. (1998), found that the presence of NOM reduced bromate formation during ozonation as it resulted in a reduction of both HOBr/OBr$^-$ and BrO_3^- concentrations. Because NOM exerts a demand for ozone and hydroxyl radicals it competes with bromide and HOBr/OBr-. Recalling Figure 1, NOM will compete for O_3 with bromide and for $^{\bullet}OH$ with HOBr/OBr-. Through a study by Westerhoff et al. (1998), the competition kinetics between NOM, Br^-, and HOBr/OBr$^-$ by O_3 and $^{\bullet}OH$ were studied through bench scale ozonation in batch reactors. Results from the competition study concluded that NOM was consumed by O_3 prior to Br^-, that $^{\bullet}OH$ consumed NOM prior to HOBr/OBr$^-$, and that O_3 oxidized BrO_2^- to BrO_3^- without consideration for NOM. NOM plays a critical role in different locations throughout the bromate formation pathway. Because reactions with NOM and ozone are rapid they tend to limit the initial direct oxidation of bromide to $HOBr/OBr^-$. However, once at the $HOBr/OBr^-$ stage in bromate formation, the reaction can proceed through hydroxyl radicals or through further direct oxidation. Oxidation by hydroxyl radicals is limited by NOM at the $HOBr/OBr^-$ stage and it was suggested that progression on this formation pathway will only occur at high $^{\bullet}OH$ concentrations or at elevated pH levels. As the formation pathway reaches bromite, NOM no longer is a sink for ozone consumption and bromate formation happens quickly (Westerhoff et al., 1998). In addition, it is suggested that the type of NOM present in water has an effect on bromate formation (Westerhoff et al., 1998; Elovitz et al., 2000). On the contrary, Najm and Krasner (1995) believe that increases in organics tend to increase bromate formation due to the increase in ozone demand and the subsequent increase in ozone dose. It was suggested that increases in DOC increase bromate formation through the need to increase ozone dose to meet a target residual ozone concentration (Najm and Krasner, 1995). Another supporting study evaluated the O_3-to-DOC ratio on bromate formation and found that low O_3-to-DOC ratios produced lower concentrations of bromate as the oxidant was consumed by the NOM (Song et al., 1997). Although there are two hypotheses to the effect of organics on bromate formation, they both involve the reaction with ozone providing that ozone may be the more controlling influential parameter when it comes to oxidation of organics and bromate formation.

2.2.5. Influence of Temperature on Bromate Formation

The temperature of water can have an effect on ozone and hydroxyl radicals through a change in the oxidant's half-life. Ozone decay rates increase more than an order of magnitude between the temperatures of 5-35°C (Elovitz et al., 2000). In addition, $^{\bullet}OH$ exposure and O_3

exposure react differently with changes in temperature. While •OH exposure seems to be independent of temperature, ozone exposure is significantly reduced with increases in temperature (Elovitz et al., 2000). It is also suggested that the temperature of the water often has a greater effect on other parameters influencing bromate formation. For example, one study found that temperature only played an important role at high ozone doses but at low ozone doses changes in temperature had little to no affect on bromate formation (Galey et al., 2004). From a water treatment standpoint, ozone exposure is necessary to meet disinfection requirements. It is likely that at elevated temperatures, an increase in ozone dose would be necessary to meet the disinfection requirements due to the decrease in ozone depletion as proven by Elovitz et al. (2000). The increase in ozone dose, then, may increase bromate formation. Temperature can also affect the reaction kinetics and the $HOBr/OBr^-$ stage of the bromate formation pathways. Decreases in temperature, reduce reaction rates and reduces the acidity constant leading to a reduction in the amount of bromate that can form (Legube et al., 2004).

2.2.6. Influence of Bromide Concentration on Bromate Formation

Increases in bromide in ozonated water results in increases in bromate formation (Krasner et al., 1993; Shukairy et al., 1994; Najm and Krasner, 1995). High bromide concentrations, in general, do not increase ozone demand but do, however, provide a higher concentration available for oxidation (Shukairy et al., 1994; Najm and Krasner, 1995). In a study conducted by Shukairy et al. (1994), five different ozone doses were applied to two different levels of bromide in water. While maintaining other parameters like pH, DOC, and temperature constant in a pilot scale experiment, it was found that increases in bromide concentration caused increases in bromate at constant ozone dose. Even at the lowest ozone dose applied, the highest bromide concentration water produced bromate at levels exceeding the MCL (Shukairy et al., 1994).

2.3. Further Research Needs

Although the literature review provided a vast amount of knowledge concerning influential parameters on bromate formation, it is important to consider the limitations of the studies included. First, most studies considered the influence of parameters through bench or pilot scale tests and did not test their results on a full-scale system. Second, most studies considered pH values between 6.0-8.5 as this is the most common pH used during water disinfection. Very few, if any studies, evaluated bromate formation at a pH of 10 or 11 which is consistent with the water disinfection pH at the Moorhead WTP. Third, few studies looked at the effects of blending surface water and groundwater for ozone disinfection, which is also consistent with the Moorhead WTP. Generally, the research efforts considered each source separately or used deionized water spiked with the appropriate water quality parameters like bromide and organics.

CHAPTER 3. MOORHEAD WTP TREATMENT PROCESS

The Moorhead WTP, located in Moorhead, Minnesota, supplies water to over 48,000 people; covering the city of Moorhead itself as well as the city of Dilworth and Oakport Township in Minnesota. During the 2012 year, the facility treated approximately three to four million gallons per day (MGD) of water in the winter and six to seven MGD of water in the summer. Moorhead has the ability to treat 16 MGD of flow through the use of two treatment facilities. However, the 10 MGD facility is the facility that is utilized primarily. The water treatment plant in Moorhead has been in place since 1895 and has undergone many improvements since its beginning. In the plant's early days, it was purely a pumping station that sent water from the Red River to the city residents. In 1910, wells were drilled in the city and the community members were allowed to collect water. As well water began to replace the warmer river water, more wells were drilled in 1947 in the Buffalo Aquifer. In 1951, a water treatment plant was completed to soften the hard Buffalo Aquifer water. As the population of Moorhead grew, the well water source began to deplete and the city looked at using river water again. In 1961 a new lime softening treatment plant was constructed to incorporate both the surface and groundwater sources. Finally, in 1995 the plant underwent a reconstruction phase adding a 10 MGD facility that was equipped with the newest technology in water treatment; utilizing ozone for disinfection and taste and odor control. This research project focused specifically on the 10 MGD capacity plant that was constructed in 1995. Overall, the current treatment process includes the following: river/well mixing, sedimentation with lime/soda ash softening, primary ozone disinfection, multi-media filtration, and secondary chloramine disinfection. (Moorhead Public Service, 2013)

3.1. Source Water Options for Drinking Water Treatment

The Moorhead WTP is a two source water treatment facility. Both surface water and groundwater serve as water sources for treatment. The surface water utilized is the Red River of the North and the groundwater sources stem from wells that draw water from the Buffalo Aquifer and the Moorhead Aquifer. The Red River is the primary water source for the treatment facility while the groundwater sources are used to supplement the river water when needed. Each water source contains its own water quality characteristics providing the water plant with the ability to use the different water sources to their advantage in different circumstances.

3.1.1. Red River Water Characteristics

The Red River of the North is a surface water source that runs north through Fargo/Moorhead into Manitoba, Canada. Due to its location in the Northern United States, the river is subject to great temperature swings throughout the change in seasons. Over the course of the 2011 year, the river water saw temperatures near freezing to as high as 27°C. As shown in Figure 3 the river water temperature is highest in the summer months of June to August and at its lowest in the winter months where the temperature is near 0°C. These changes in temperature have an effect on operational parameters at the Moorhead WTP.

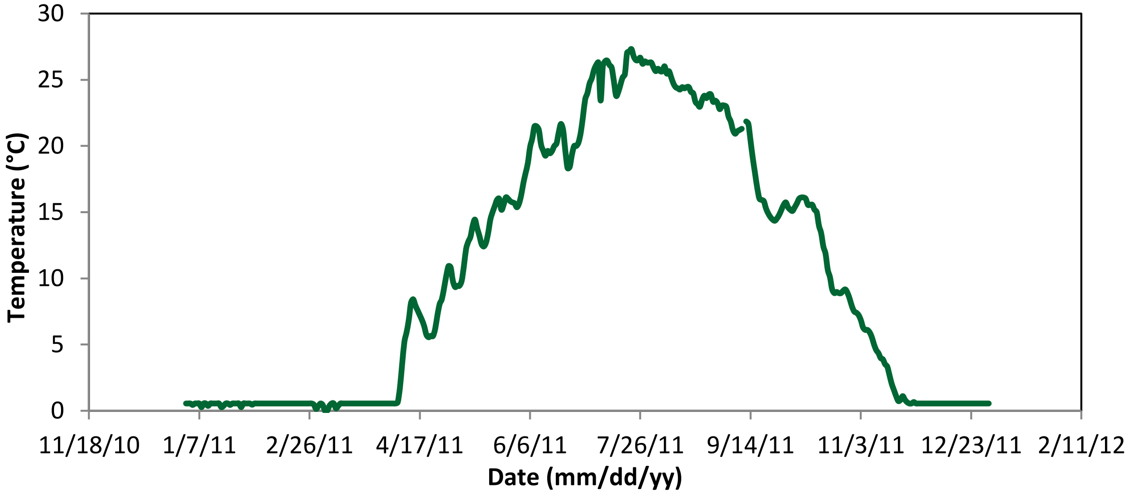

Figure 3: 2011 Red River temperatures at Moorhead WTP river influent pipeline

Another variable that is seen in the river water entering the treatment plant is the organic matter as recorded as TOC. TOC changes in the river water are seasonal but also change more sporadically due to changes in weather patterns. For instance, a rain event after a long dry period will cause a spike in TOC in the river as overland runoff collects particles and washes into the river. In addition, during spring snow melt, overland runoff again will flow into the river and cause gradual increases and decreases in the TOC concentration. In addition, in the early spring, upstream dam discharges for flood control can cause temporary increases in the TOC and hardness in the Red River. Throughout the course of the 2011 year (Figure 4), the river TOC averaged near 10.3 mg/L with a maximum of 12.6 mg/L and a minimum of 6.3 mg/L. During times of increased TOC values in the river water, the Moorhead WTP has the option of using groundwater to supplement the river water to reduce the overall TOC in the water used for drinking water treatment.

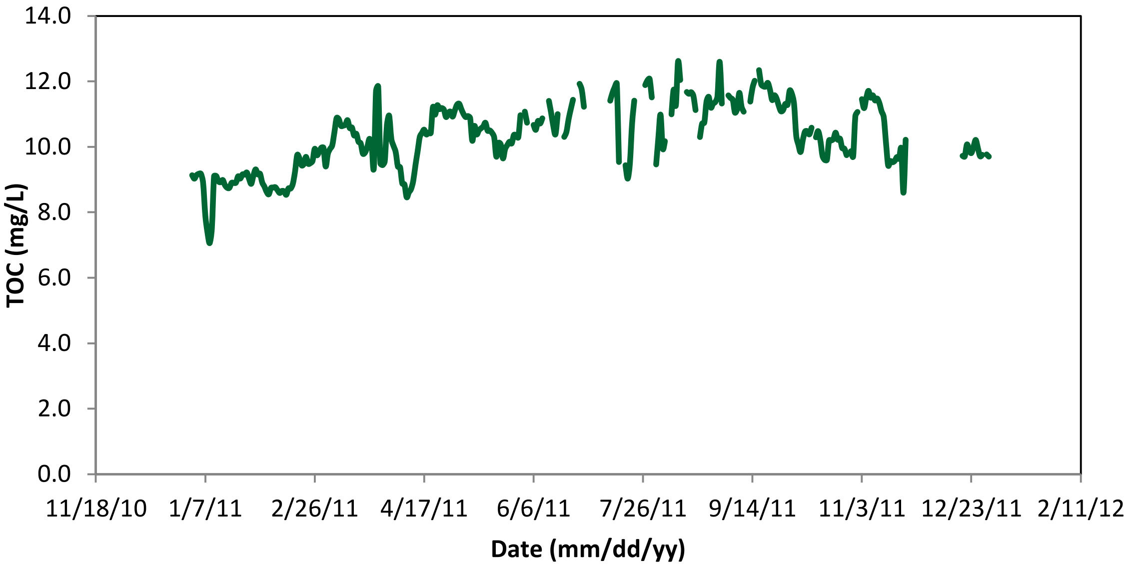

Figure 4: 2011 Red River TOC at Moorhead WTP river influent pipeline

Due to the surface water quality of the Red River, many other water quality changes occur in the form of hardness, alkalinity, and turbidity. Abrupt changes in these water quality parameters can be combated by the water plant operators through groundwater addition as groundwater is much more stable than river water in terms of water quality.

3.1.2. Groundwater Sources and Characteristics

The Moorhead WTP utilizes seven wells from two aquifers, Moorhead and Buffalo Aquifers, at three main locations: Moorhead Aquifer Wells, North Buffalo Aquifer Wells, and South Buffalo Aquifer Wells. As shown in Figure 5, wells 6 and 6B are located near the treatment facility and draw water from the Moorhead Aquifer, wells 8, 9 and 10 are located further East in the South Buffalo Wells location, and wells 1 and 2 are located in the North Buffalo Wells location. It is important to note, however, that there is only one Buffalo Aquifer, but Moorhead has wells in two different locations within the aquifer titled, North Buffalo and South Buffalo.

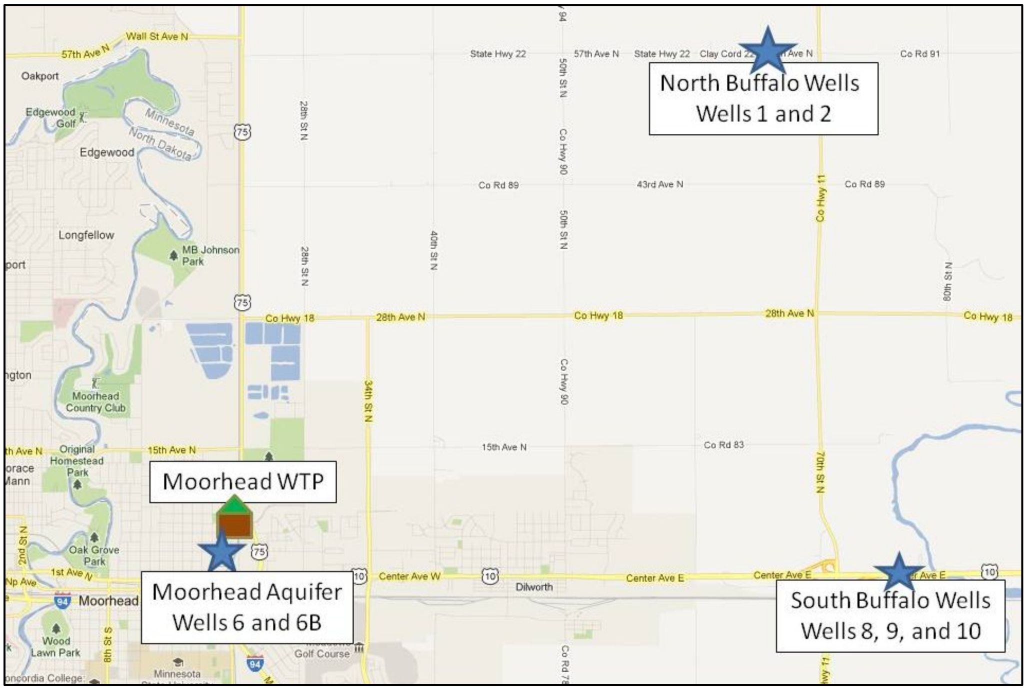

Figure 5: Moorhead well locations

As a treatment facility, the Moorhead WTP numbers their wells for ease of use by the operators. Table 4 may be used for a representation of the well numbers and the respective aquifers in which they draw water.

Table 4: Aquifer and well designation for Moorhead WTP

Aquifer	Well Name
Moorhead Aquifer	6 and 6B
Buffalo Aquifer- South location	8, 9 , and 10
Buffalo Aquifer- North location	1 and 2

A unique aspect of the Moorhead WTP is that the facility has the ability to alter the influent water quality through the use of the different water sources. The difference in locations of the wells provide for the change in water quality between the different water sources. The Moorhead Aquifer is classified as a confined aquifer as the soil above the water table in this aquifer consists of 100 ft or more of low permeable clay and till. It was determined to have no direct vertical hydraulic connection with surface water and therefore is recharged through other means than simply precipitation and infiltration (Bureau of Reclamations, 2005). The Buffalo Aquifer, an unconfined aquifer, is vulnerable to contamination based on transport of contaminants through the soil layers. The aquifer soils vary with location. The predominant aquifer material ranges in size from fine sand to gravel. Recharge of the Buffalo Aquifer stems primarily from snow melt and rain, however, near the Moorhead well locations, the surface water recharge in this area can include the Buffalo River, South Buffalo River, and Red River of the North, depending on hydraulics (Wolf, 1981).

The average depths of the Buffalo and Moorhead Aquifers were found to vary depending on location within the aquifer. Well depths were found using the County Well Index from the Minnesota Department of Health as shown in Table 5 (MDH, 2009).

Table 5: Well depths

Well	Aquifer	Unique Well #	Depth (ft)
6	Moorhead	241492	273
6B	Moorhead	437645	280
1	Buffalo-North location	511085	205
2	Buffalo-North location	511086	243
8	Buffalo-South location	222049	122
9	Buffalo-South location	222050	114
10	Buffalo-South location	222051	124

Water quality characteristics, such as organic contents, hardness, and bromide concentrations, can change between the different groundwater sources. The Moorhead WTP has the ability to select certain wells to use to be of most benefit to their treatment process in different situations.

Concerning organics, the groundwater sources have a TOC concentration less than the Red River water source. For the 2011 year, the groundwater TOC values averaged at 2.9 mg/L with a maximum of 4.0 mg/L and a minimum of 1.8 mg/L. Groundwater TOC values (Figure 6), as well as most water quality parameters, remain nearly constant over the course of a year. Aquifers have a much slower recharge rate than surface water bodies providing for less changes in water quality parameters. In addition, the layers of soil above the water table act as a filter, providing for less TOC and turbidity, but adding to hardness in most cases. The sample location for well water is located in the influent pipeline in the Moorhead WTP making the analyzed TOC samples in Figure 6 a mixture of the different wells used for plant influent well flow for that day.

Another parameter that varies by groundwater well location is water hardness. In terms of hardness, both total hardness and calcium hardness were measured for each groundwater source. In comparing the different aquifers, the Moorhead Aquifer contained much softer water than the Buffalo Aquifer. Due to the softer nature of the water, the Moorhead WTP often utilizes the Moorhead Aquifer during times of hard water conditions in the Red River as a supplement. The respective hardness values can be seen in Table 6.

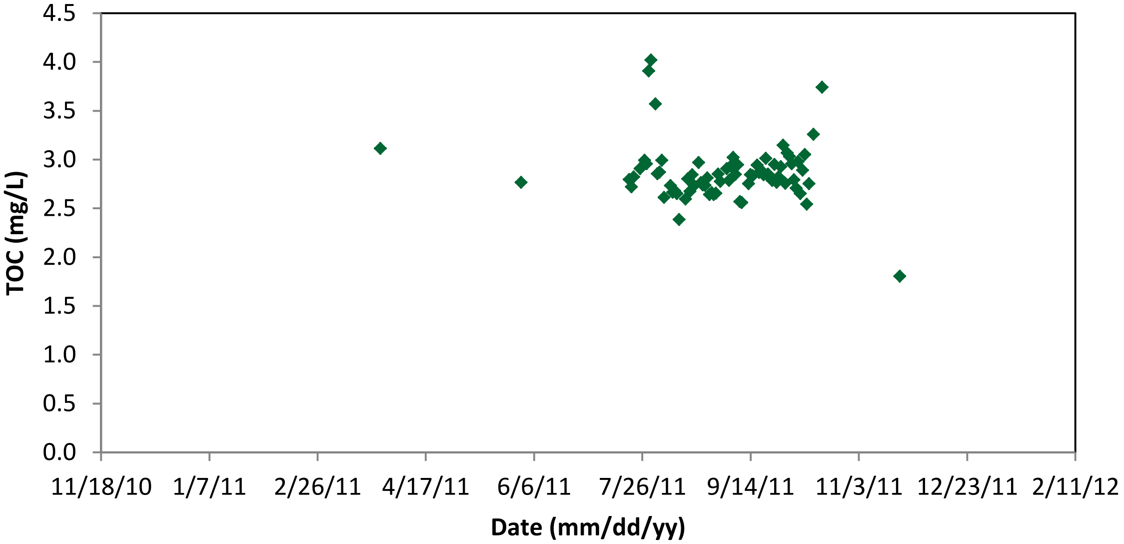

Figure 6: 2011 groundwater TOC at Moorhead WTP well influent pipeline

Table 6: Water hardness values for Moorhead WTP wells

Well Number	Aquifer Source	Total Hardness (mg/L $CaCO_3$)	Ca Hardness (mg/L $CaCO_3$)
6	Moorhead Aquifer	196	128
1	Buffalo-North location	544	336
2	Buffalo-North location	508	288
8	Buffalo-South location	520	332
9	Buffalo-South location	384	252
10	Buffalo-South location	356	284

3.2. Drinking Water Treatment Process

Water enters the plant through the plant inlet structure. In this structure, the groundwater mixes with the river water in an agitation channel and ferric sulfate ($Fe_2(SO_4)_3$) is added. This additive helps in the coagulation process. It is also at this point where wasted water from filter backwashes and decant water from the softening sludge ponds re-enter the plant. The inlet chamber is marked as point 1 in Figure 7.

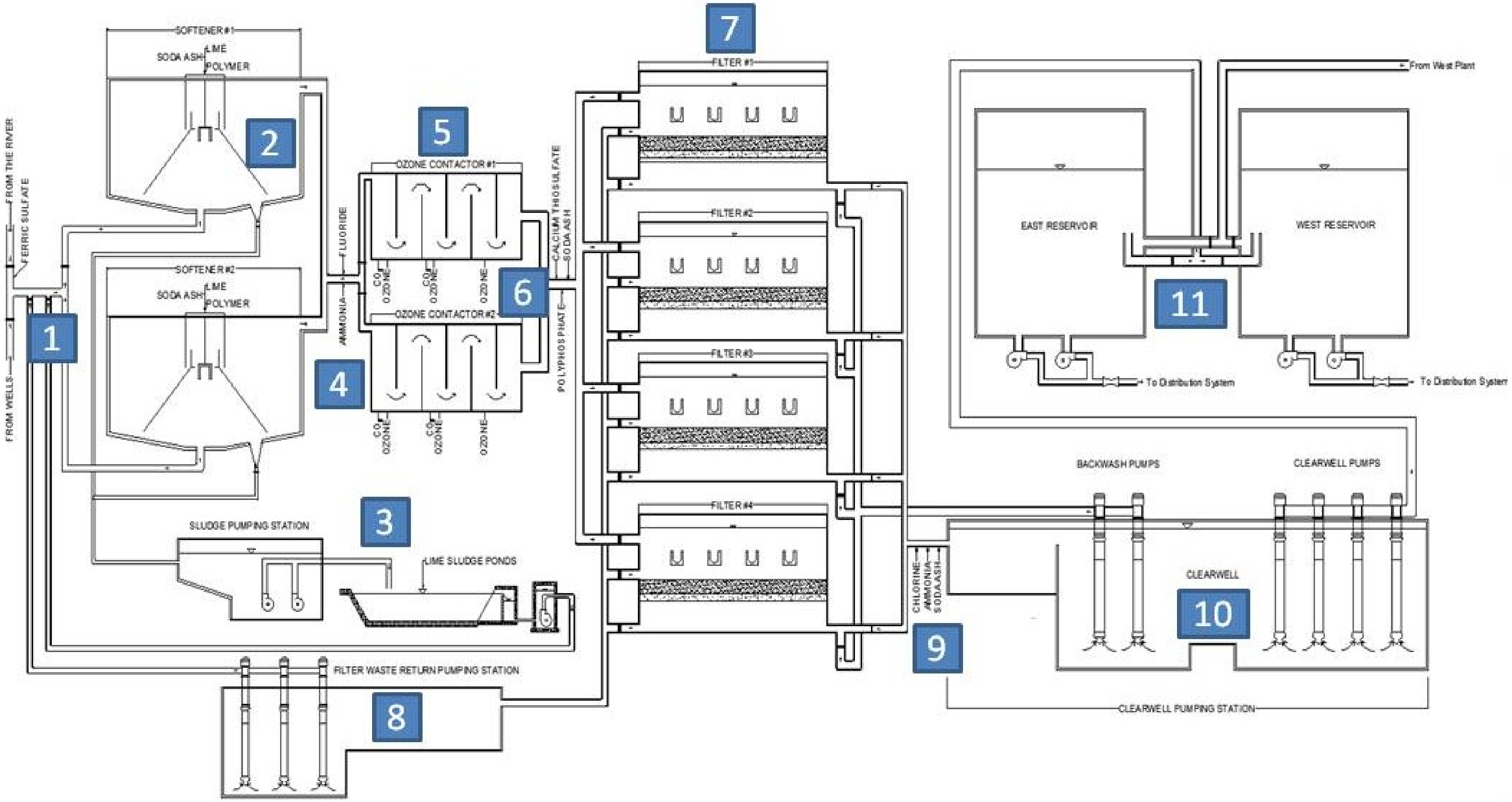

Figure 7: Process flow diagram

Next, the lime/soda ash softening process begins and includes the addition of lime ($Ca(OH)_2$), and soda ash (Na_2CO_3) to remove carbonate and non-carbonate hardness from the source water. The softening process takes place in two softening basins. The basins have a designed surface area of 50 ft by 50 ft or 2500 ft^2 both of which hold a water depth of approximately 18 ft, providing for a maximum water volume of about 336,600 gallons each (JMM Consulting Engineers Inc., 1992). Each basin can treat about 5 MGD and is equipped with a center mixer and perimeter rake. During high demand, flows greater than 5 MGD, both softening basins are used. During low demand times, flows less than 5 MGD, one of the basins is used. A polymer is also added to the center of the basin during this process to thicken the sludge blanket that is produced from the coagulation process. The location of the chemical additions in the softening process can be seen as number 2 in Figure 7. The rake and mixer components of the softening basin also help to develop the sludge blanket that improves the chemical reactions that take place in the water. Ultimately, as the sludge blanket builds it is slowly pumped out of the basin through the bottom of the system and discharged to sludge ponds as shown as number 3 in Figure 7. At the end of this process the softened water generally has a total hardness between 90 and 110 mg/L as $CaCO_3$ and has a pH in the range of 10.6 to 11.3. Fluoride is also added at this stage to achieve a final concentration of about 1.1 to 1.2 mg/L to improve the dental health of the consumers. During the summer months, as the water leaves the softening process, operators have the option of adding ammonia to the softened water to hinder the bromate formation in the next stage of treatment, ozone disinfection. These two chemical additions are located at number 4 in Figure 7.

After softening, the water passes into the ozone disinfection chambers, marked as number 5 in Figure 7. The Moorhead WTP is equipped with two disinfection chambers and each chamber is divided into six cells (A-F) through the use of baffles. Similar with the softening basins, each contact chamber was designed with a capacity 5 MGD. Again, one chamber is used during low flow conditions and two chambers are utilized when the flow increases to greater than 5 MGD. The baffles in the contact chambers allow the water to be ozonated at different levels of pH as will later be discussed. Both carbon dioxide (CO_2) and ozone are applied to the water through fine bubble diffusers that are placed on the floor of the contact chamber in Cells A, C, and E. In general, however, CO_2 is primarily added in Cells A and C but the ability to feed into Cell E is available. As the water flows through Cells E and F final disinfection occurs and the water leaves the contact chambers and enters the filters.

In the winter months, during colder temperatures, calcium thiosulfate is added to the water prior to filtration to remove any excess ozone in the water to protect the filters and improve taste as shown as number 6 in Figure 7. During warmer temperatures in the summer months this addition is not necessary because at these temperatures the reaction rate of ozone is much higher and excess ozone residual does not occur. Sodium polyphosphate ($(NaPO_3)_6$; sodium hexametaphosphate) is also added at this stage as the disinfected water leaves the ozone disinfection chambers to stabilize the water aiding in reduction of scaling and copper/lead leaching throughout the distribution network.

Filtration at the WTP includes a duel media biofiltration system, shown as number 7 in Figure 7. The filter media consists of two feet of anthracite and one foot of sand that sits atop an under drain system. Anthracite, having a lower specific gravity sits above the sand layer. During the summer months, a biological growth provides a biofiltration system and assists in the removal of organic compounds from the water. This aspect of the filters decreases as the water temperature decreases and biological growth diminishes. The WTP is equipped with four filters that each receives an equal amount of water from the ozonation process. The filters are each 13 ft in length and 26 ft in width providing for a surface area of 338 ft^2 (JMM Consulting Engineers Inc., 1992). Depending on the flow through the plant, the filtration rate alters. Based on the designed capacity of 10 MGD, each filter has a loading rate of 5.1 gpm/ft^2(JMM Consulting Engineers Inc., 1992). Each filter is also backwashed approximately every 80-90 hours through the use of an air scour system and produces a backwash rate of 5400 gpm. The backwashed water is collected and sent to a reclaim pit that ultimately sends the water back to the head of the plant to be reused as shown as number 8 in Figure 7.

After final filtration, the water is chlorinated to provide a secondary disinfectant that will remain in the water throughout the distribution system. Also at this stage, ammonia is added to form chloramines. In times of warmer temperatures, especially in the summer months, soda ash is added after filtration to maintain a pH of approximately 9.0 to 9.3 to protect the distribution system pipe networks. All chemical additions can be seen in number 9 in Figure 7. After chlorination and ammonia addition water enters a clearwell. The clearwell at the Moorhead plant holds approximately 68,000 gallons of water, shown as number 10 in Figure 7 (JMM Consulting Engineers Inc., 1992). As the water achieves its appropriate contact time in the clearwell, it enters one of the two reservoirs that the Moorhead plant utilizes. The reservoirs are classified as the East and West reservoirs and they have a capacity of 2.4 million gallons and 3.1 million gallons of water respectively (JMM Consulting Engineers Inc., 1992). The reservoirs provide the source of water for the distribution system and are depicted as number 11 in Figure 7.

3.3. Operational Controls for the Drinking Water Treatment Process

As stated previously, the ozone disinfection chamber is split into 6 sections labeled A-F. However, considering the under-over flow pattern of the water, the chamber can be divided into three sections, as shown in Figure 8. The ozone contact chamber is used for disinfection as well as pH adjustment and each section has its own designed task to meet these requirements. As a lime and soda ash softening plant, the Moorhead WTP requires recarbonation in order to return the water pH to a consumable level after the softening process. The Moorhead WTP utilizes CO_2 for pH depression. CO_2 as well as ozone are applied in the ozone disinfection process through fine bubble diffusers located at the bottom of the disinfection chambers that bubble in a countercurrent direction.

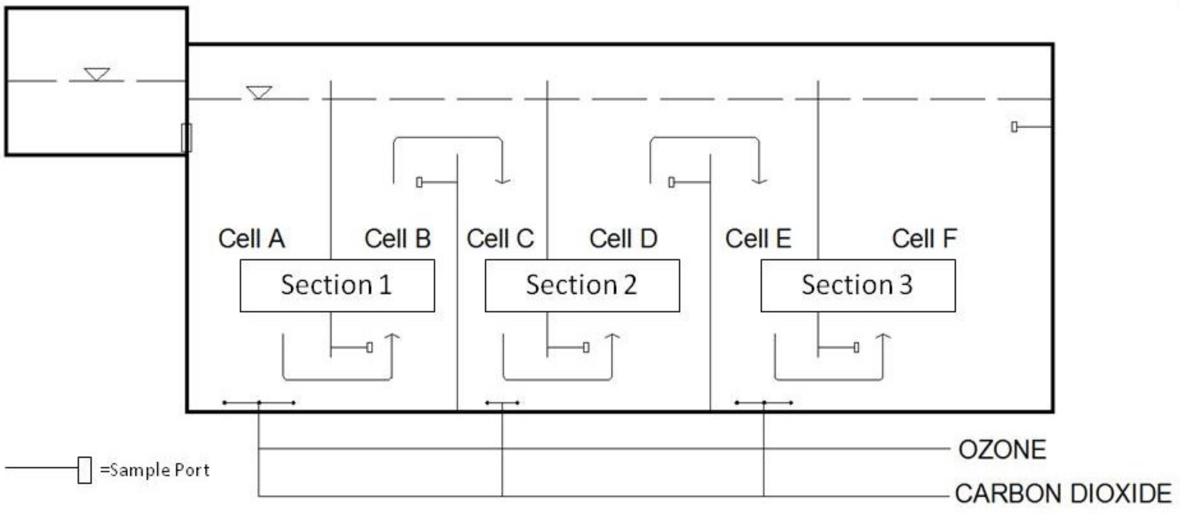

Figure 8: Ozone contact chamber section divisions

3.3.1. pH Depression in the Ozone Contact Chambers

pH in the ozone chambers at the Moorhead WTP is controlled differently depending on the season. During the winter, when the water temperature is low, ozone reaction rate is low leading to lower ozone demand. A higher pH is maintained in Section 1 of the ozone chambers to provide taste and odor removal. By leaving the pH at a high level initially in the ozone chambers, generally a pH of approximately 11, hydroxyl radicals are produced that aide in advanced oxidation to remove many of the organic compounds in the water during the first section of the ozone chamber. In the winter months, recarbonation is carried out in Cell C of the ozone chambers (Figure 8). CO_2 flow to Cell C is controlled to achieve the specific pH level at the influent of Cell D, which is also the pH of the water that ultimately is sent to the distribution system. As an operational parameter, ozone residual in Sections 2 and 3 is controlled by adjusting ozone dose to meet CT requirements.

During the summer months the pH depression methodology is changed. At this time of season, the water temperature increases, increasing reaction rates and ozone demand. Subsequently, to meet CT requirements, ozone dose needs to be increased to provide the necessary residual for disinfection. As the regulations for bromate were put into place for treatment facilities utilizing ozone, the Moorhead WTP began to lower the water pH earlier in the disinfection process to reduce the necessary ozone dose and try to reduce their bromate formation. Also, the lower pH aided in the facility's ability to maintain an ozone dose within the equipment's operating range. In the summer, CO_2 is added in Cell A through fine bubble diffusers and the pH is monitored for control at the influent to Cell B (Figure 8). By lowering the pH earlier in the process, ozone is less reactive and less ozone is consumed during the disinfection process. To meet the necessary disinfection requirements during this time of year, instead of raising and lowering the ozone dose, as is done in the winter, the pH is adjusted to acquire the necessary ozone residual for disinfection. If the ozone residual increases high enough the ozone dose can be lowered and disinfection requirements are still maintained. However, through the summer method, the finished pH of the water is often lower than desired for distribution, and the pH must be increased again. In this case, the pH is increased after filtration by adding soda ash to the clearwell. By this addition, the pH once again reaches the pH level of near 9.0 to 9.3 that the Moorhead WTP maintains for distribution.

3.3.2. Ozone Disinfection

Considering the task of disinfection, the ozone chamber is also used to bubble ozone gas through the fine bubble diffusers. As was similar for pH depression, each section of the contact chambers has its own responsibility. As a water treatment facility, the Moorhead WTP falls under the requirements of the EPA's Surface Water Treatment Rule (USEPA, 1989) for disinfection requirements and is monitored by the Minnesota Department of Health (MDH). Under this rule, the Moorhead WTP is required to inactivate 3-log (99.9%) Giardia and 4-log (99.99%) virus (USEPA, 2011). According to the MDH, the conventional treatment at the plant accounts for 2.5-log Giardia credit and 2-log virus credit for removal (MDH, 1995). This leaves 0.5-log Giardia removal and 2-log virus removal needed from the ozone disinfection process. With ozone disinfection, the 2-log virus requires a higher contact time (CT) value than the 0.5-log Giardia, causing the 2-log virus to be the designing factor for CT calculations (Table 7).

Table 7: Ozone inactivation of Giardia cysts and viruses (adapted from USEPA, 1999)

Inactivation (log)	Temperature (°C)					
	1	5	10	15	20	25
			Giardia cysts			
0.5	0.48	0.32	0.23	0.16	0.12	0.08
			Viruses			
2.0	0.90	0.60	0.50	0.30	0.25	0.15

To assist in the operation of the treatment plant, a SCADA system was implemented and CT calculations were incorporated to allow operators to maintain the disinfection required for appropriate removal of Giardia cysts and viruses. As part of the SCADA system, a required CT is compared to an actual CT to maintain compliance.

The required CT calculation is determined using EPA CT tables for ozone disinfection at different temperatures (USEPA, 1999). An example of an EPA table can be seen in Table 7. For simplicity in a SCADA system, the CT values for virus inactivation by ozone were plotted for 2-log inactivation against temperature and a linear representation of the line was determined (Figure 9). A linear estimation line greater than the actual curve was chosen to ensure compliance is always maintained. The linear line was then programmed into the SCADA system to determine the required CT at any given water temperature found in the ozone chamber.

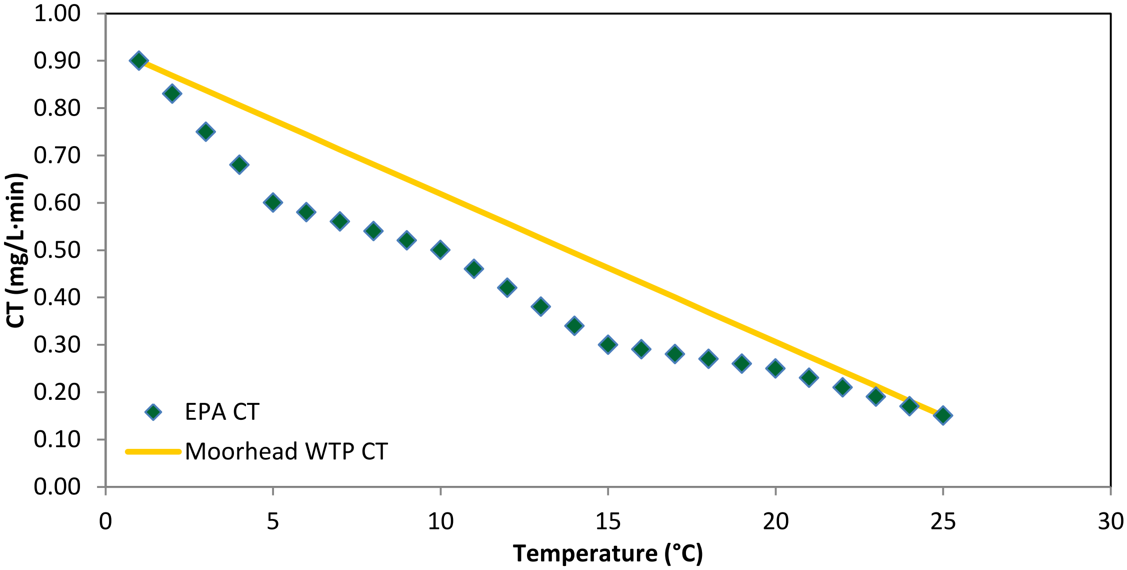

Figure 9: Moorhead WTP SCADA CT estimate

The actual CT is calculated to ensure compliance with disinfection regulations. The actual CT achieved is a summation of CT gained from Sections 2 and 3 in the ozone chambers at the Moorhead WTP (Figure 8). Section 1 is not considered for disinfection credits at the Moorhead WTP due to the high pH in this section and the likely low to non-existent ozone residual as a result. To determine the actual CT achieved within the contact chamber, ozone residual, water flow, and temperature are recorded. The actual CT found within the ozone disinfection chamber is calculated through the following equation:

$$Actual\ CT = 0.7\left[C_2\left(\frac{V_2}{Q_2}\right) + C_3\left(\frac{V_3}{Q_3}\right)\right] \tag{5}$$

where C (mg/L) is ozone residual measured at the effluents of Sections 2 and 3, V (gallons) is the volume of each section, and Q (gpm) is the water flow rate through the ozonation chambers. A baffling factor of 0.7 is applied as determined by the MDH (1995). Using Equation 5, the final unit for CT is found to be mg/L·min.

Residual ozone is measured using online ozone analyzers that are calibrated using the Indigo Method. The residual ozone concentrations are recorded through SCADA, along with the flow through the contact chamber at that time. The volume of Section 2 is calculated through the summation of Chambers C and D. The entire contact chamber is 17 ft tall and 15 ft wide and the individual lengths of Cells C and D are 5 ft and 9 ft respectively as shown in Figure 10 (JMM Consulting Engineers Inc., 1992). This provides for a volume of flow of 3570 ft^3 or 26,775 gallons. The volume of Section 3 is calculated through the summation of Chambers E and F. Chambers E and F have lengths of 6 ft and 13 ft respectively (Figure 10) providing for a volume of 4845 ft^3 or 36,338 gallons as diagramed in Figure 10 (JMM Consulting Engineers Inc., 1992). Flow through the ozone chamber is determined through a flow meter.

With these values recorded by the SCADA system, an actual CT value is known at all times of operation at the Moorhead WTP. The actual CT can then be compared to the EPA required CT estimate (Figure 9) to ensure the ozone disinfection process is achieving the necessary inactivation requirements.

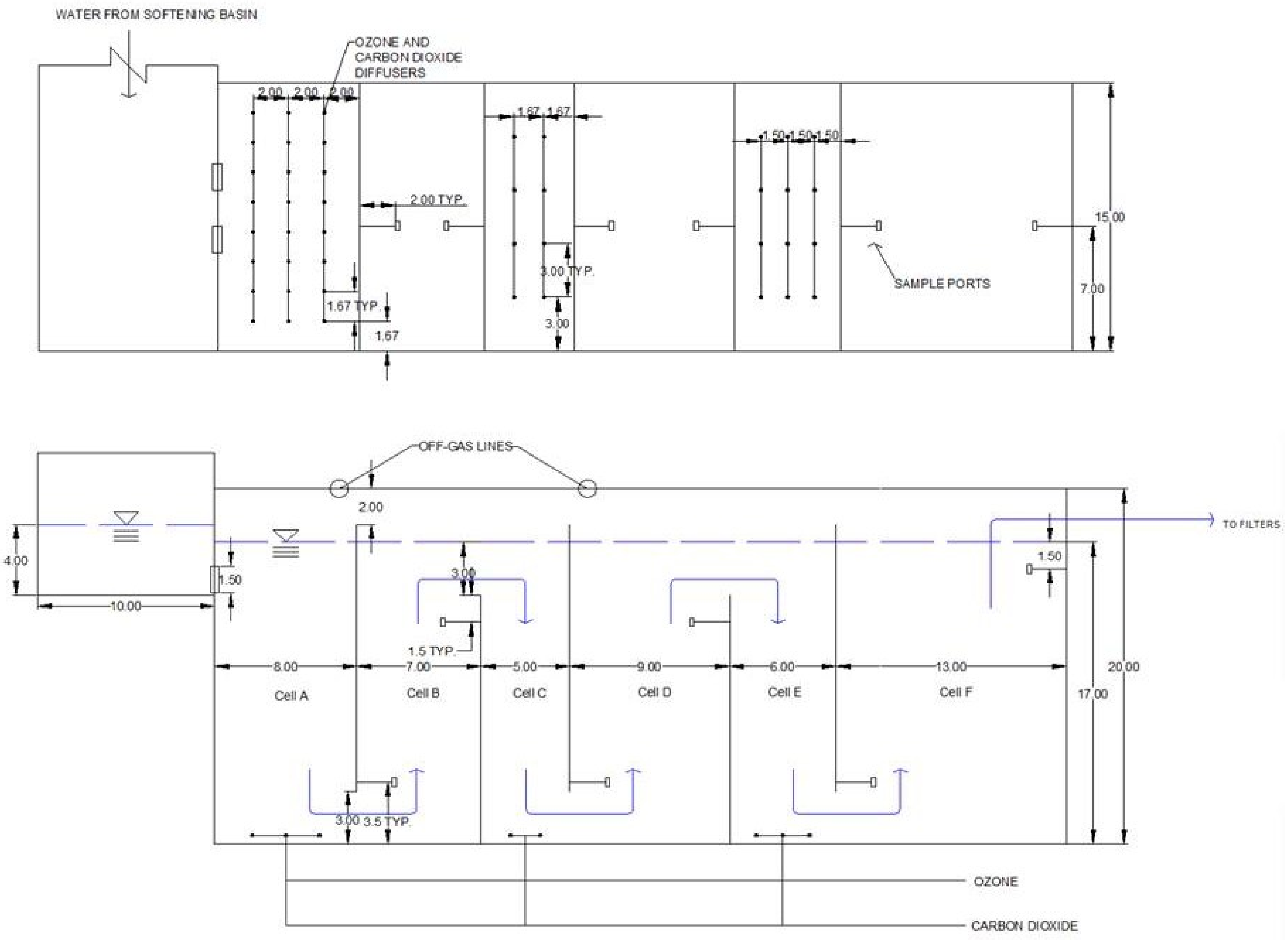

Figure 10: Ozone chamber details

3.4. Historical Data Analysis

In order to better understand the operational conditions that occur at the Moorhead WTP, a historical analysis was conducted. The analysis included review of plant operational data from past years to gain a better sense of operational conditions and changes in operational techniques that occur throughout the change in seasons. These changes included alterations to river and well flow and their respective impact on parameters such as temperature and TOC. In addition, seasonal changes in TOC were also analyzed.

3.4.1. River and Well Flow

The Moorhead WTP utilizes both surface water and groundwater sources for drinking water treatment. In general, the surface water from the Red River is used as the primary water source and groundwater sources are used to supplement the river water. As part of the historical analysis it was important to discover patterns and trends in the use of surface water and groundwater throughout the change in seasons. The source water chosen for treatment will have an impact on temperature, TOC, and bromide concentrations impacting bromate formation potential.

During a typical year at the Moorhead WTP, river water is used as the main source of water throughout the entire year. However, there are three main purposes to why the treatment plant may use well water flow: to increase produced water, to decrease finished water temperature, and to improve water quality prior to treatment. Figure 11 displays the river and well flow during the 2011 year. As shown in the figure, well flow is minimal in the winter months when river water quality is generally good and stable. The increase of well water use in the spring in 2011 was due to the extended period of flood levels in the Red River that year and the Moorhead WTP’s inability to clean the river intake screen. For other years, it is likely that well flow may be added in the spring season due to the poor river water quality during spring runoff and the duration of well use at this time is generally less than was needed in 2011. Well flow utilized during the summer months of 2011, did not cause an increase in total flow, and therefore was likely utilized to lower the finished water temperature instead of to meet consumer demand. However, during drier summers, well flow may be used to increase the total flow to meet the increase in demand during the summer months. As the winter returns, the well flow again returned to minimal use in 2011 as with other years in the past.

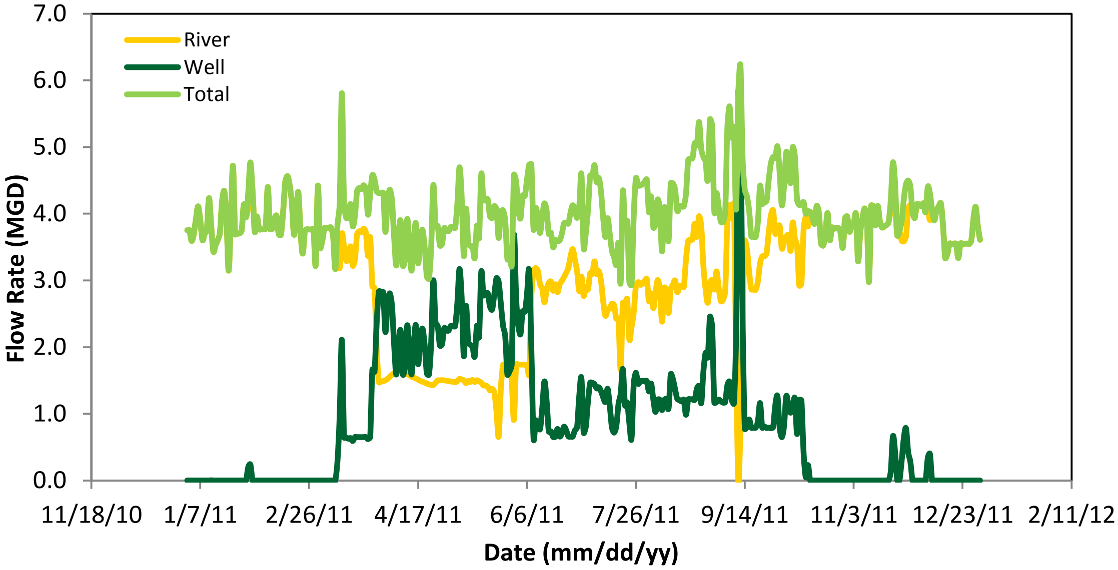

Figure 11: 2011 river and well flow

3.4.2. Demand Changes

The first purpose of groundwater use occurs during times of increased water demand. When the flow rate capacity of the river pumps is met, wells are added to increase the amount of treated water. Increases in demand generally occur in the summer months in Moorhead. In most cases, the river water supplies enough flow to meet demand requirements in the winter and wells are less likely to be used. Seasonal changes in water use are fairly consistent from year to year. In general, the highest demands are found in the summer months and well water is needed to meet the increased requirements. From Figure 12 it can be seen that the highest water flows at the Moorhead WTP occur during the summer months of July to August and return to a lower flow rate during the winter season. This pattern was consistent for the 10 years of data that were analyzed in Figure 12 and in addition, little increase in demand has occurred between 2001 and 2011.

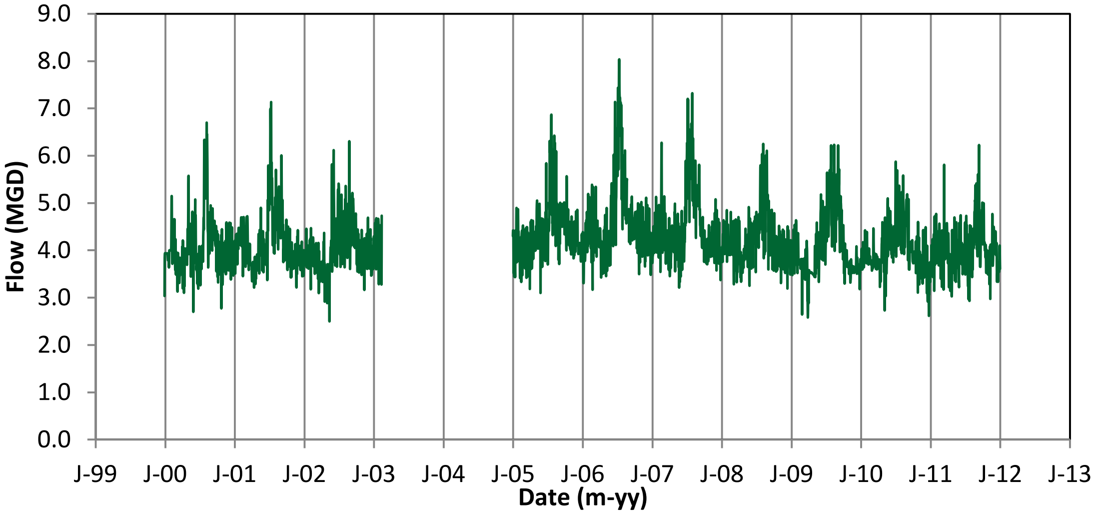

Figure 12: Treated water 2000 to 2011

3.4.3. Temperature Changes

The second reason for well water use is for temperature control. Well water is used during the summer months to meet the unique temperature requirements of some of the customers. Due to the geographical location of the Moorhead WTP in the upper Midwest of the United States, water temperature variations are seen throughout a year of data. Throughout the course of a year, the temperature of the river water changes along with the seasonal changes as shown previously in Figure 3. As the ambient temperature increases in the summer months of June to August the river water temperatures increase and the Moorhead WTP utilizes the lower temperature groundwater to lower their finished water temperature. The Moorhead WTP supplies water to industrial consumers that require a finished water temperature below 70-72°C.

In the winter months as the ambient temperature decreases the river water temperature also decreases and the resulting finished water temperature of the WTP is lowered. The variation in water temperature from river water to finished water can be seen in Figure 13.

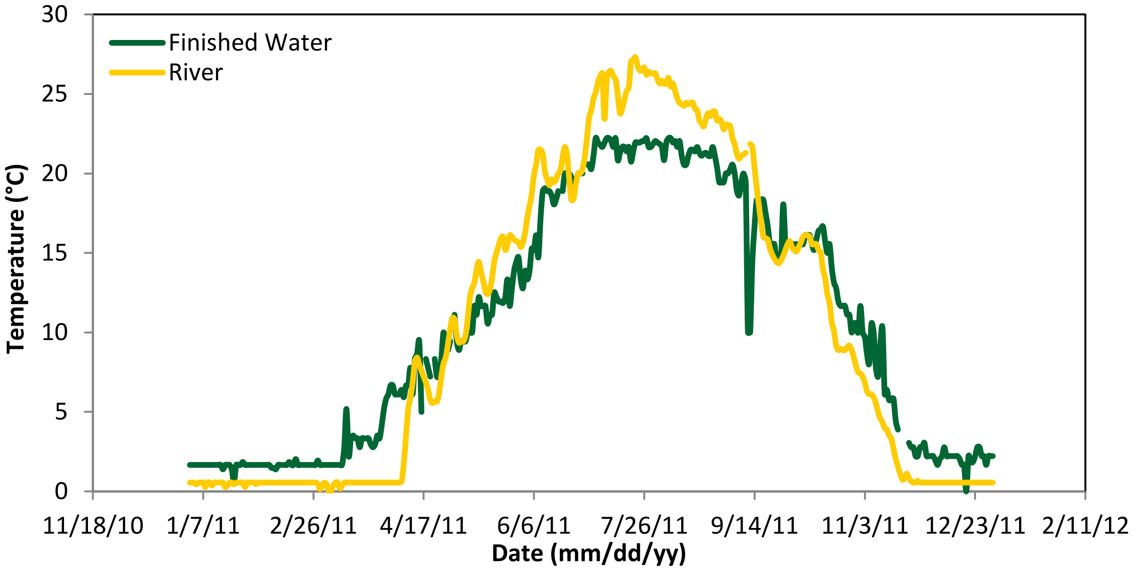

Figure 13: 2011 Red River and finished water temperatures at the Moorhead WTP

The temperature variations can be explained by the addition of cooler groundwater during the summer months as shown through the comparison between Figures 11 and 13. During the non-summer months, the water temperature was increased with the addition of the groundwater because at this time, the river water is actually cooler than the groundwater. An example of well water increasing the finished water temperature occurred between the months of February and April in 2011, shown in Figure 13. During this circumstance, it was likely that the well water flow was not used for temperature alterations but instead for water quality changes. Because the total flow in Figure 11 remained unchanged as the well flow increased and the river flow decreased, it is likely the treatment facility was using the well flow for quality changes instead of temperature changes.

3.4.4. Water Quality Changes

Thirdly, well water is used to supplement the river water flow during times of poor river water quality. Poor river water quality may include high hardness, TOC, or turbidity, all of which can be lowered using well water.

Historical data from the Moorhead WTP for the past 10 years were analyzed to understand the variations in TOC that occur seasonally and that have occurred long term. First, the source water TOCs were analyzed to discover any trending patterns that were occurring long term over the past 10 years. Over the course of the decade, no notable long-term variation in the river or well TOC was discovered. As shown through the difference between the 10 year average and the yearly averages in Figure 14 the river water yearly averages stayed close to the overall 10 year average of 9.82 mg/L. In fact, in the span of 10 years, the 10 year average and the yearly averages had an average difference of only 0.5 mg/L TOC in the Red River. The largest difference in yearly to 10 year average river TOC occurred during 2005, straying 1.25 mg/L from the 10 year average as shown in Table 8. Variations in TOC ranged from 6.24 mg/L to 16.35 mg/L over the 10 year span. Changes in Red River TOC values can be caused by rain events, precipitation patterns, and upstream activity.

The well TOC was found to be less than the Red River TOC. Over the 10 year analysis, the average well TOC value was 2.95 mg/L and there were no long-term changes in groundwater TOC values as displayed by the yearly TOC averages for the 10 year analysis in Table 9. In addition, the variations in well TOC were less than that found in the Red River. The well TOC was more consistent than the river TOC with an average difference in yearly averages from the 10 year average of 0.14 mg/L. The largest difference in TOC values also occurred during 2005 with 0.28 mg/L difference from the 10 year average.

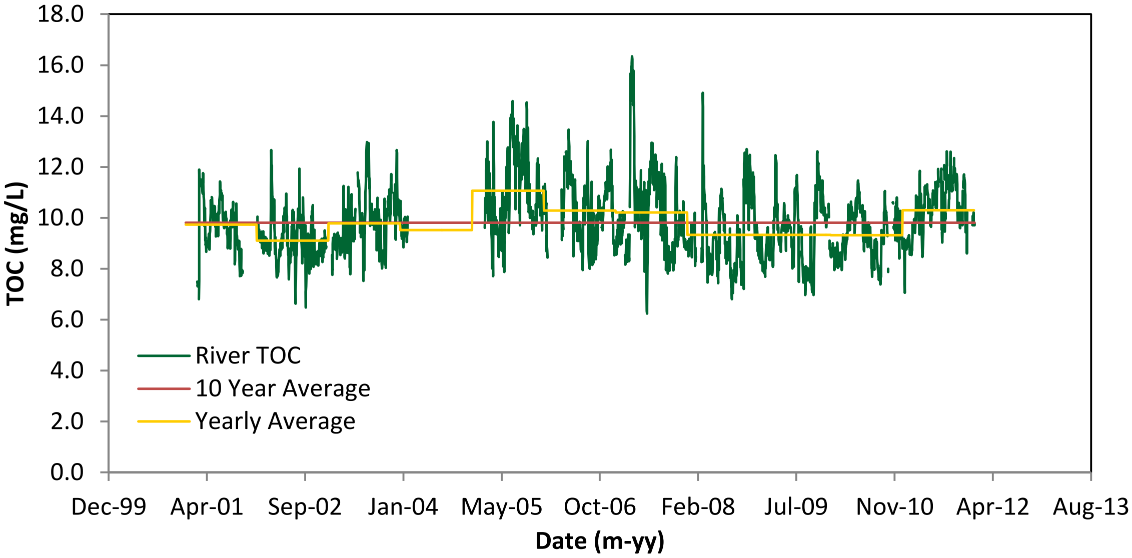

Figure 14: Red River TOC-10 years

Table 8: Red River yearly TOC averages

Year	Average TOC (mg/L)
2001	9.74
2002	9.11
2003	9.79
2004	9.52
2005	11.07
2006	10.29
2007	10.22
2008	9.34
2009	9.33
2010	9.32
2011	10.30

The range of TOC values in the groundwater sources (Figure 15) is much less than the Red River with values ranging from 1.80 mg/L to 4.53 mg/L, a span of 2.73 mg/L which is much less than the span of 10.10 mg/L found in the Red River water. Variations that were found in the well water are likely attributed to variations in measurement rather than actual water quality changes. Groundwater sources maintain water quality parameters better than surface water sources like the Red River.

Table 9: Groundwater TOC yearly averages

Year	Average TOC (mg/L)
2001	2.72
2002	2.95
2003	3.15
2004	n.a.
2005	3.23
2006	2.90
2007	3.11
2008	3.05
2009	3.08
2010	2.81
2011	2.86

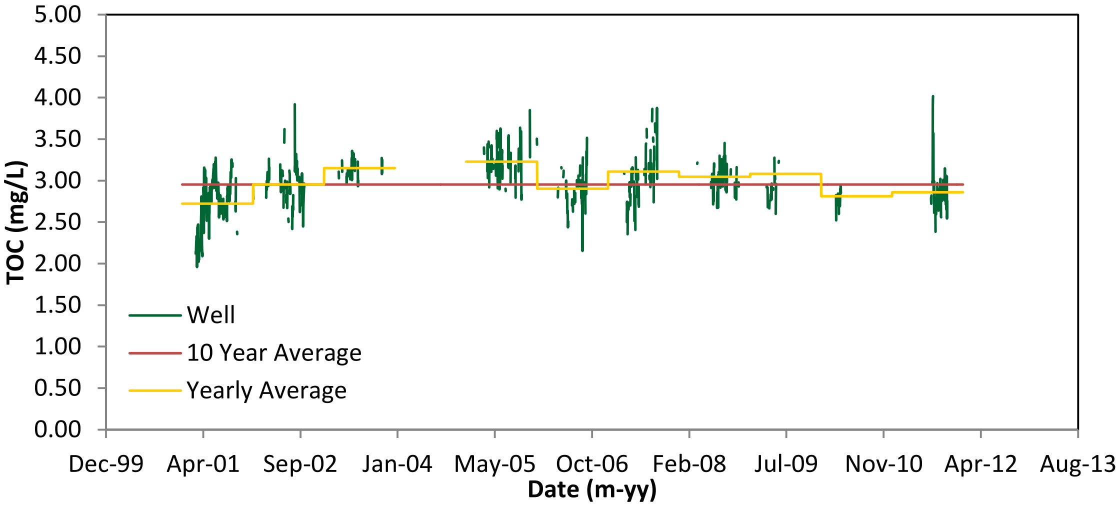

Figure 15: Well TOC-10 years

At the Moorhead WTP, at times of high demand or poor river water quality, well water is added to the river water flow. In Figure 16 is the TOC in the river compared to the TOC in the mixture of water at the influent of the WTP. Historically, the Moorhead WTP does not test the TOC at the mixing of the water sources but instead from each water source individually so a mass balance calculation was conducted for the influent mixture TOC. It was observed that the use of well water can reduce the influent TOC values.

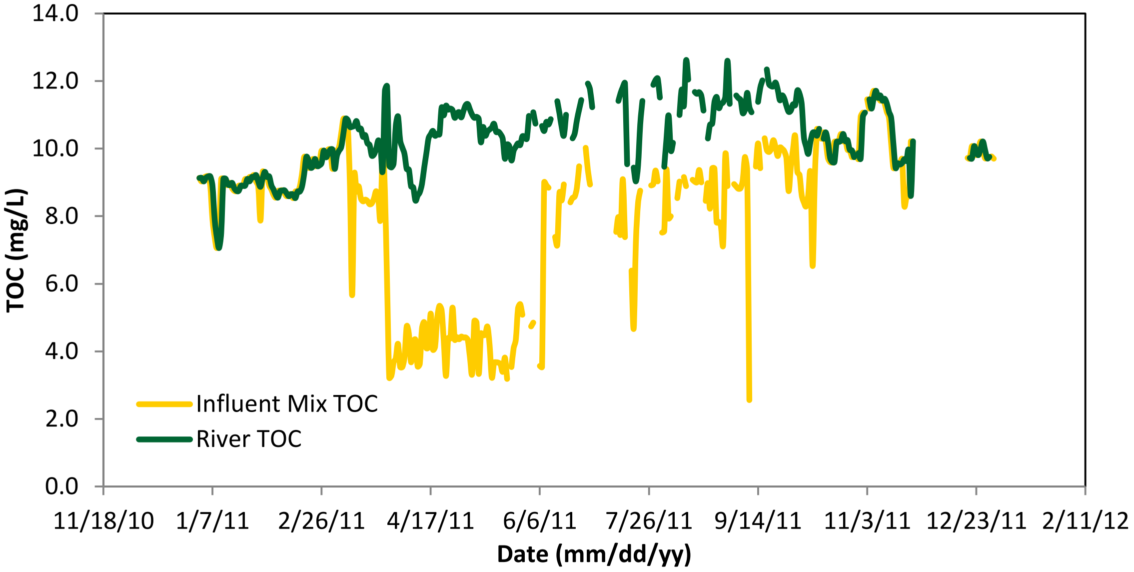

Figure 16: 2011 Red River and influent mix TOC at Moorhead WTP

To determine TOC removal efficiency in the sedimentation and softening processes at the treatment plant, a 10 year variation in plant influent water TOC compared to the softening effluent TOC was developed as shown in Figure 17. The water leaving the softening basin is ultimately the water that enters the ozone chamber making it helpful to understand the changes in TOC during the softening process. In the 10 year span, the softening basin averaged a removal of 3.46 mg/L of TOC with a minimum and maximum removal of near 0.00 and 7.94 mg/L respectively. On average, for the 10 year span, the softening process removed 51% of the TOC with a standard deviation of 0.08% or 1.18 mg/L TOC. There were no long term variations in the efficiency of TOC removal in the softening process however, seasonal changes in TOC removal occurred (Figure 18). Lesser reduction values occurred in the summer months during the times of increased well flow and subsequently decreased influent mix TOC.

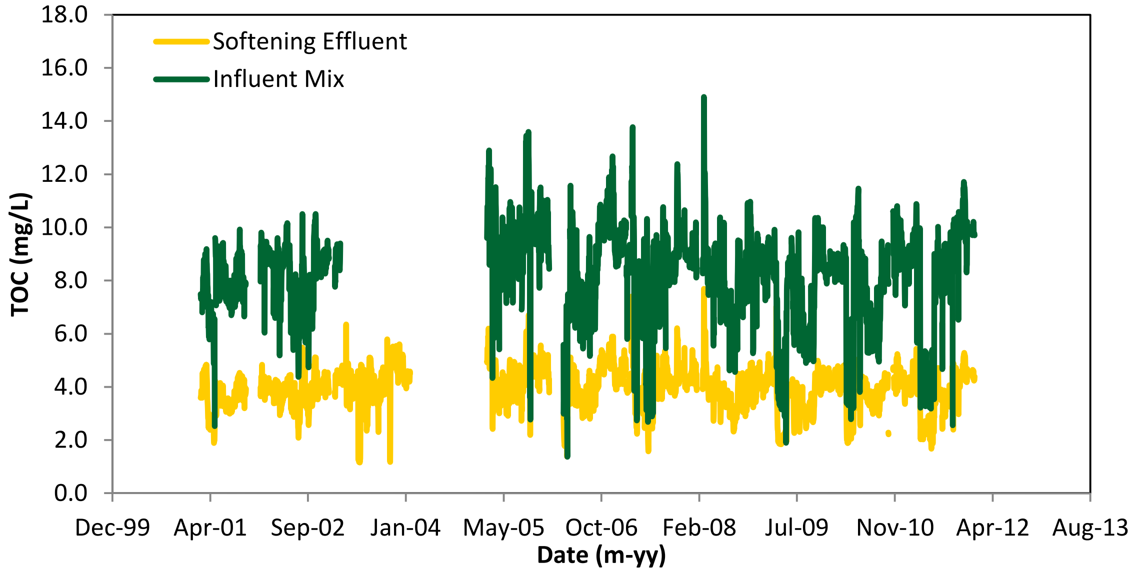

Figure 17: Influent mix TOC compared to softening effluent TOC

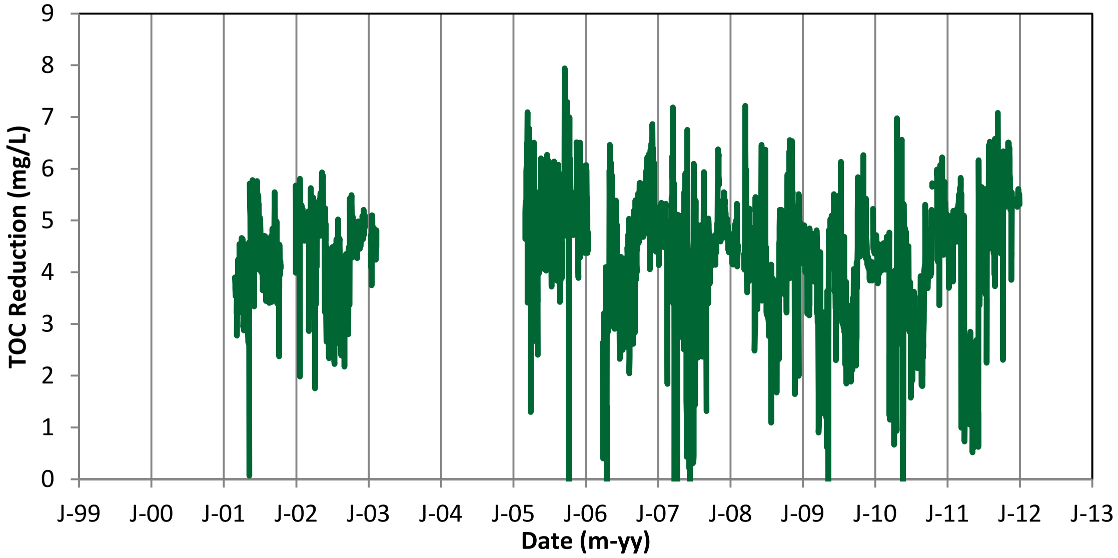

Figure 18: Softening process TOC reduction

The next source of TOC removal occurs in the ozone chamber during the disinfection process. Because ozone is a very reactive oxidant, it can be used to remove organic matter from the water. Figure 19 displays the TOC removal that occurs in the ozone chamber. This value was found by subtracting the TOC concentration in the ozone chamber effluent sample from that found in the ozone chamber influent sample. Over the last 10 years, the organic removal capabilities within the ozone chamber at the Moorhead WTP have not changed substantially. On average, over the 10 year span, the TOC removal obtained was 0.23 mg/L. The removal efficiency of the disinfection system is much less than that obtained through the softening process. The yearly pattern of TOC removal (Figure 20) seems to follow a cyclic pattern. This is likely attributed to the higher removal efficiencies in the summer months with the increase in temperatures. As the temperatures begin to decrease, removal amounts also decrease.

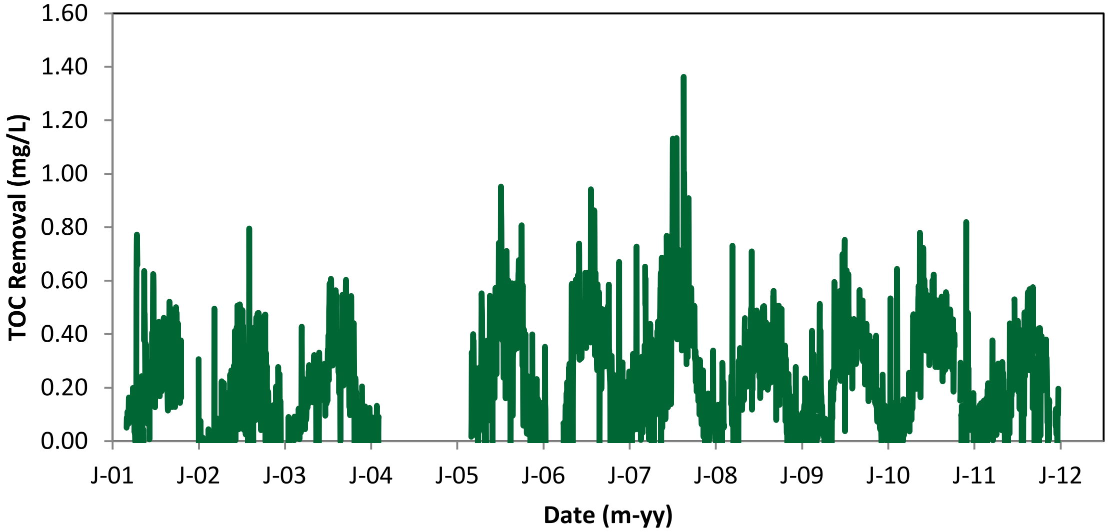

Figure 19: TOC removal in ozone chamber-10 year

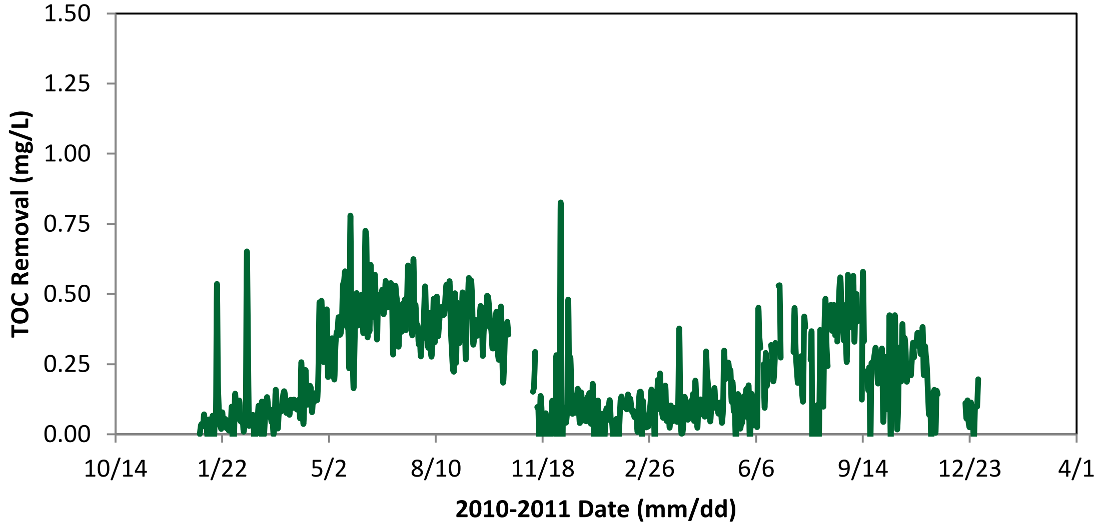

Figure 20: TOC removal in ozone chamber-2010-2011

3.4.5. Bromide Concentrations

Very little bromide data was available for a historical analysis. However, the Fargo WTP, in Fargo, ND also utilizes the Red River for a source water and collected bromide data from the river. The Fargo WTP river intake screen is located very close to the Moorhead WTP intake screen allowing for the data to be considered. During the 2011 year, the bromide concentration found in the Red River averaged 0.056 ppm with a peak concentration of 0.091 ppm and a minimum concentration of <0.021 ppm. From Figure 21, it appears that the bromide concentration is fairly constant with a possible increase from 2010 to 2011, but there is not enough data to make a strong conclusion.

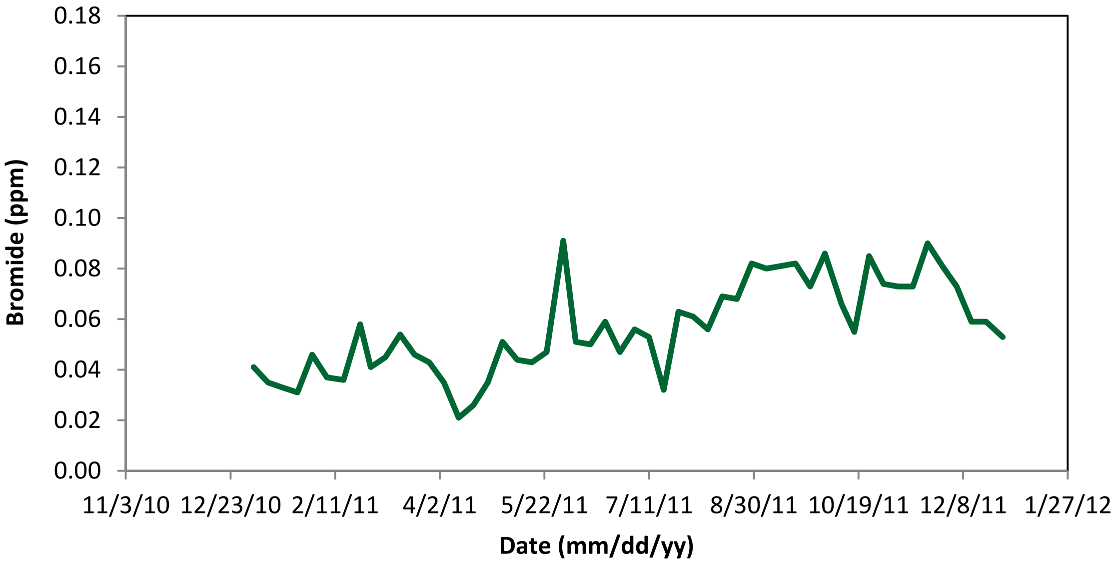

Figure 21: Red River bromide at Fargo WTP influent (analysis by Fargo WTP)

CHAPTER 4. METHODS AND MATERIALS

The methods used in the investigation of bromate formation at the Moorhead WTP were maintained throughout the sampling period. Methods developed and materials used for bromide sampling, bromate sampling, bromide and bromate sample analyses, and tests of water quality parameters are presented in this chapter.

4.1. Sample and Analysis Method

Water samples were collected from different locations throughout the Moorhead WTP to capture changes in influent water quality to effectively study the ozone disinfection system specifically. A nine month sampling period was conducted to allow for seasonal changes to be displayed. During the sampling period the effects of source water selection, TOC, UV254, temperature, ozone dose, and pH were analyzed. Separate sampling plans were developed for bromide and bromate samples.

4.1.1. Bromide Sampling

Bromide samples were taken from the following locations: Red River, groundwater sources, ozone chamber influent, and ozone chamber effluent. The sample locations can be seen in Figure 22. Sampling frequency varied throughout the research project, however, bromide and bromate samples were always taken at the same time. During the summer months, sampling was conducted on a daily to every-other-day basis. Towards the end of the sampling period the frequency of sampling was gradually decreased to weekly sampling. The river bromide samples were collected on a weekly basis by the Fargo WTP from its river influent pipeline. Groundwater source bromide samples were collected from the well sites specifically and from the groundwater influent pipeline to the Moorhead WTP. Groundwater sampling was sporadic as sampling could only occur at times when the Moorhead WTP was pumping that specific well into the plant for treatment.

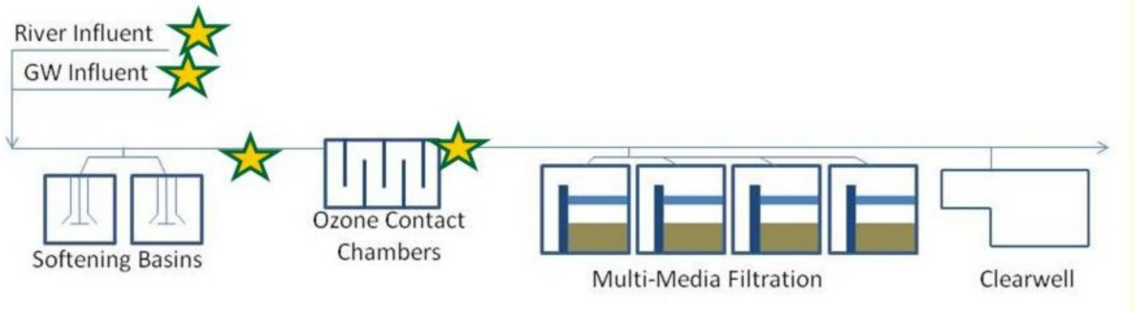

Figure 22: Bromide sample locations

The purpose of sampling the influent water sources for bromide concentration is to provide the Moorhead WTP with knowledge on the background bromide concentrations for all of their source water options. As discussed in Chapter 2, influent bromide concentrations to an ozonation system can influence bromate formation and will be of concern. In addition, quantifying the bromide concentrations by source water will aide in the optimization process of the Moorhead WTP for bromate minimization.

Prior to ozonation, bromide concentrations may have changed during the processes of source water mixing and softening.   Bromide sampling at ozone chamber inlets was needed to evaluate the change of bromide concentration after mixing and softening processes. Ozone chamber influent samples were collected more frequently than the source water samples due to the importance of understanding the initial bromide concentration which could have a direct impact on bromate formation in ozone chambers.

Ozone chamber effluent samples were collected on the same frequency as ozone chamber influent sample collection. The purpose of sampling the ozone effluent sample is to obtain the amount of bromide left after the disinfection process and oxidation at the WTP is complete. The ozone effluent bromide sample analysis will provide for a quality control check point.

The bromide concentration was not analyzed in other locations such as within the ozone chambers, at the filter effluent, or within the finished water in the clearwell.

4.1.2. Bromate Sample Plan

Bromate samples were taken from the following locations within the ozone chamber: Section 1 effluent, Section 2 effluent, and Section 3 effluent. These sample locations are labeled with stars in Figure 23. Bromate sampling frequency varied throughout the research project depending on bromate concentration and source water selection. During the beginning of the sampling period, sampling was conducted on a daily to every-other-day basis and on the same days that bromide samples were collected from the ozone influent and effluent points. Towards the end of the sampling period the frequency of sampling gradually decreased to weekly sampling. As the sampling period progressed and bromate concentrations were found to decrease, the sampling frequency was decreased. Also, during times of all well flow in the latter half of the sampling period, ozone application was removed from the treatment process and sampling did not occur.

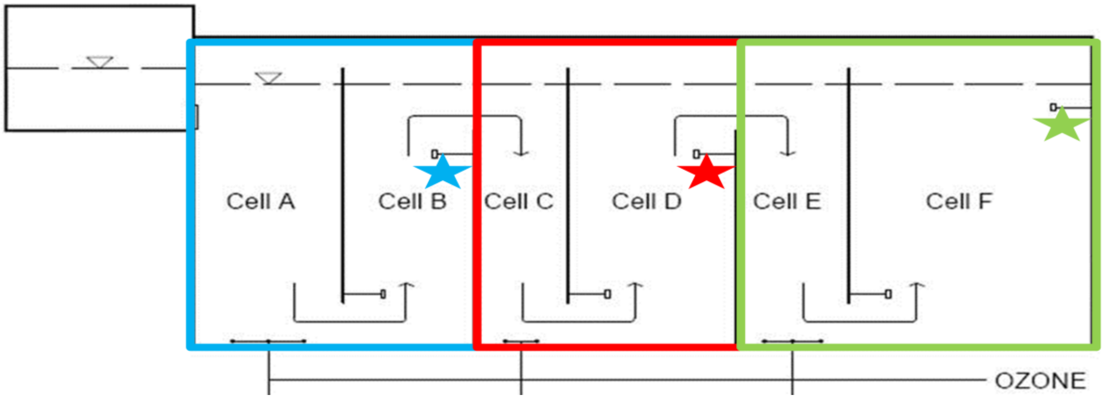

Figure 23: Bromate sample locations

The bromate sampling points in the ozone chamber refer to the effluent points of each section in the chamber. As the chamber is constructed to allow for an under-over flow pattern, and ozone is applied in a countercurrent fashion, there is an influent and effluent point to each section of the chamber. Bromate sampling locations were chosen to effectively capture the amount of bromate that is formed after each application of ozone. As shown in Figure 23, ozone is applied in Cells A, C, and E. Consequently, samples were collected just prior to the next addition of ozone in the disinfection process.

The bromate concentration was not sampled in other locations such as the influent water sources, ozone chamber influent, filter effluent, or clearwell. The influent sources will not be tested for bromate because bromate concentrations were in general, not detected in source waters (Shukairy et al., 1994). The ozone chamber influent samples are the resulting water after the softening and sedimentation process. This location was not sampled as it was assumed that the bromate at this stage in the treatment process would be negligible as no oxidative processes precede ozonation. The filter effluent was not analyzed for bromate concentrations because at this point the oxidation process is complete and therefore the filter performance is out of the scope of this research project.

4.2. Bromide and Bromate Sample Analysis

Bromate and bromide concentrations were measured using a DIONEX ICS-3000 Ion Chromatography (IC) system at the Moorhead WTP. Bromide analysis followed the USEPA Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography (Hautman and Munch, 1997). Bromate analysis followed the USEPA Method 302.0: Determination of Bromate in Drinking Water Using Two-Dimensional Ion Chromatography with Suppressed Conductivity Detection (Wagner et al., 2009). The overall analysis batch organization and method procedures for sample analyses were kept consistent throughout the research project.

4.2.1. Sample Preservation, Storage, and Hold Time

Following the requirements of Method 300.1 (Hautman and Munch, 1997), the bromide samples were not preserved but the samples were stored between a temperature of 2-5°C as suggested. Following the requirements of Method 302.0 (Wagner et al., 2009) the bromate samples were preserved using Ethylenediamine (EDA) and stored between a temperature of 2-5°C as suggested. For both bromide and bromate, sample holding time was set at 28 days (Hautman and Munch, 1997; Wagner et al., 2009).

4.2.2. Quality Control and Quality Assurance

Both the bromide and bromate sample analysis methods follow a similar organization for batch analysis. A maximum of 20 samples are included in each batch for analysis. An analysis batch is defined by the precision and accuracy requirements. In each batch, the analysis included an initial calibration check standard, continuing calibration check (CCC) standard, laboratory reagent blank (LRB), and a laboratory fortified blank (LFB). Also, for every 10 field samples analyzed in the batch at least one laboratory fortified matrix and a duplicate were included as required. The duplicate may pertain to a laboratory duplicate or a duplicate of the laboratory fortified matrix (Hautman and Munch, 1997; Wagner et al., 2009).

At the beginning of an analysis, a calibration curve is analyzed to determine the minimum reporting limit (MRL) for the analysis. The MRL is defined as the lowest standard analyzed and recovered at 50-150% for bromate and 75-125% for bromide (Hautman and Munch, 1997; Wagner et al., 2009). Based on the MRL, low background noise in the instrument analysis is verified through the analysis of LRB and LFB. LFBs also aide in determining the accuracy of the analysis and consistency in the laboratory procedures. Percent recoveries for MRL, LRB, and LFB for each method are found in Table 10.

Table 10: Precision and accuracy requirements (Hautman and Munch, 1997; Wagner et al., 2009)

	Bromate Criteria	Bromide Criteria
Sample Description	Recovery or Difference Requirement	
CCC at MRL	50-150%	75-125%
Laboratory Reagent Blank	≤ 1/3 MRL	< MRL
Laboratory Fortified Blank	≤ 2(MRL) 50-150%	≤ 10(MRL) 75-125%
	≥ 2(MRL) 80-120%	≥ 10(MRL) 85-115%
Fortified Samples	≤ 2(MRL) 50-150%	≤ 10(MRL) 75-125%
	≥ 2(MRL) 80-120%	≥ 10(MRL) 85-115%
Duplicate Samples	≤ 2(MRL) ±20%	≤ 10(MRL) ±20%
	≥ 2(MRL) ±50%	≥ 10(MRL) ±10%
CCC	80-120%	≤ 10(MRL) 75-125%
		≥ 10(MRL) 85-115%

During the analysis, accuracy is determined by percent recovery using fortified blanks, fortified samples, and calibration checks, while precision is analyzed through percent difference using laboratory duplicates. Equations 6-8 are used to define the difference between these parameters. In Equation 6, I_c represents the initial concentration, or the first sample of the duplicate set, analyzed while D_c represents the concentration found in the analysis of the duplicate sample. Equation 6 is applied to the sample duplicates that are included in every batch during the analysis to determine precision. In Equation 7, C_s represents the fortified sample concentration while C is the sample concentration without fortification and s is the concentration of analyte in the fortified sample. Equation 7 is applied to all fortified samples that are included in every analysis batch to determine accuracy of the analysis. In Equation 8, the actual yield is the value obtained by the IC analysis and the theoretical yield is the concentration of the standard solution. Equation 8 is applied to the calibration curve as well as the calibration checks that are included in every analysis batch to determine accuracy (Hautman and Munch, 1997; Wagner et al., 2009).

$$\% \, Difference = \frac{I_c - D_c}{[(I_c + D_c)/2]} \times 100\% \qquad (6)$$

$$\% \, Recovery \, (FORT) = \frac{C_s - C}{s} \times 100\% \qquad (7)$$

$$\% \, Recovery \, (NO \, FORT) = \frac{Actual \, Yield}{Theoretical \, Yield} \times 100\% \qquad (8)$$

Table 10 contains the defined requirements for the difference and recovery percentages. For both the bromide and bromate method, the percentage required is often based on the MRL. The quality control measurements for each analysis batch for both bromide and bromate samples are included in the appendix. Calibration, standard solution preparation, and fortification solutions were prepared by the Moorhead WTP Laboratory.

4.3. Tested Water Quality Parameters

Throughout the sampling period, certain water quality parameters were tested for each bromide and bromate sample collected. The parameters tested included: pH, temperature, and organic content. Organic content was analyzed through the parameters of TOC as well as UV254. pH and temperature were analyzed through the use of a ROSS Combination pH Electrode, TOC was analyzed with a TOC instrument class 2 designated by the Elevated Temperature/Catalyzed/Persulfate/Wet Oxidation/Nondispersive Infrared Detection using an OI Analytical model 1010 (Potter and Wimsatt, 2003). UV254 was analyzed using a Hach Spectrophotometer.

4.4. Recorded Sample Parameters from SCADA

Because samples for this research project were collected from a functioning water treatment facility, the use of the SCADA system was used to record parameters at the time of sampling. The recorded values included applied ozone dose, ozone residual, and source water flow.

CHAPTER 5. RESULTS

Bromide concentrations, bromate concentrations, water quality parameters, and their relationships with each other provide the results of this research. Bromide concentrations were analyzed for all source waters at the Moorhead WTP and bromate concentrations were determined within the ozonation chamber. Through these concentrations and a comparison of water quality parameters, relationships were determined for bromate influential parameters.

5.1. Bromide Concentrations

Bromide concentrations were analyzed at the following points in the treatment process: Red River, wells, ponds, ozone chamber influent, and ozone chamber effluent.

5.1.1. Groundwater Sources Bromide Concentrations

Well water samples were collected at the wells to determine the bromide concentration in each location. Multiple samples were taken from each location throughout the sampling period so an average value was determined. However, due to the difficulty of obtaining a sample from well 6B within the Moorhead Aquifer, samples were collected at the groundwater influent line at the water plant during times when well 6B was utilized. Once at the influent of the water plant, the groundwater is a mixture of all wells in use at that time. A mass balance was then used to determine the approximate bromide concentration of well 6B.

As discussed previously (Chapter 3), the Moorhead WTP utilizes seven wells from three main locations: Moorhead Aquifer Wells, North Buffalo Aquifer Wells, and South Buffalo Aquifer Wells. For all groundwater sources, the bromide concentrations have been found to vary depending on the location of the groundwater source. In general, the Moorhead Aquifer was found to have a higher bromide concentration than the Buffalo Aquifer. Through sampling and analysis at the Moorhead WTP, bromide concentrations were found to be 0.068, 0.078, and 0.084

ppm for wells 8, 9, and 10 in the Buffalo South location. For wells in the Buffalo North location, wells 1 and 2 were found to contain bromide concentrations of 0.065 and 0.050 ppm respectively. The highest bromide concentrations were found in the Moorhead Aquifer in wells 6 and 6B with a bromide concentration of 0.287 and 0.304 ppm respectively. Table 11 displays average bromide concentrations for all groundwater sources analyzed.

Table 11: Groundwater bromide concentrations

Well	Location	# of Samples	Standard Deviation	Bromide (ppm)
1	Buffalo-North location	5	0.031	0.065
2	Buffalo-North location	3	0.034	0.050
6	Moorhead Aquifer	2	0.016	0.287
6B	Moorhead Aquifer	2	0.009	0.304
8	Buffalo-South location	4	0.025	0.068
9	Buffalo-South location	6	0.029	0.078
10	Buffalo-South location	2	0.051	0.084

It was determined that the Moorhead Aquifer had the highest bromide concentrations near an average between wells 6 and 6B of 0.30 ppm. The Buffalo aquifer had a lesser concentration of bromide, averaging between wells 1, 2, 8, 9, and 10 to be around 0.07 ppm.

5.1.2. Red River Bromide Concentrations

For the 2012-2013 sampling period from May to January, the average bromide concentration in the Red River was 0.05 ppm with a maximum concentration of 0.07 ppm and a minimum of 0.03 ppm (Figure 24). Bromide concentrations were collected and analyzed by the Fargo WTP as part of an ongoing research effort at that plant. The Fargo WTP had a more extensive set of data points for bromide concentration in the Red River so the Fargo data was selected for use. No trends in the river bromide were observed during the time of sampling.

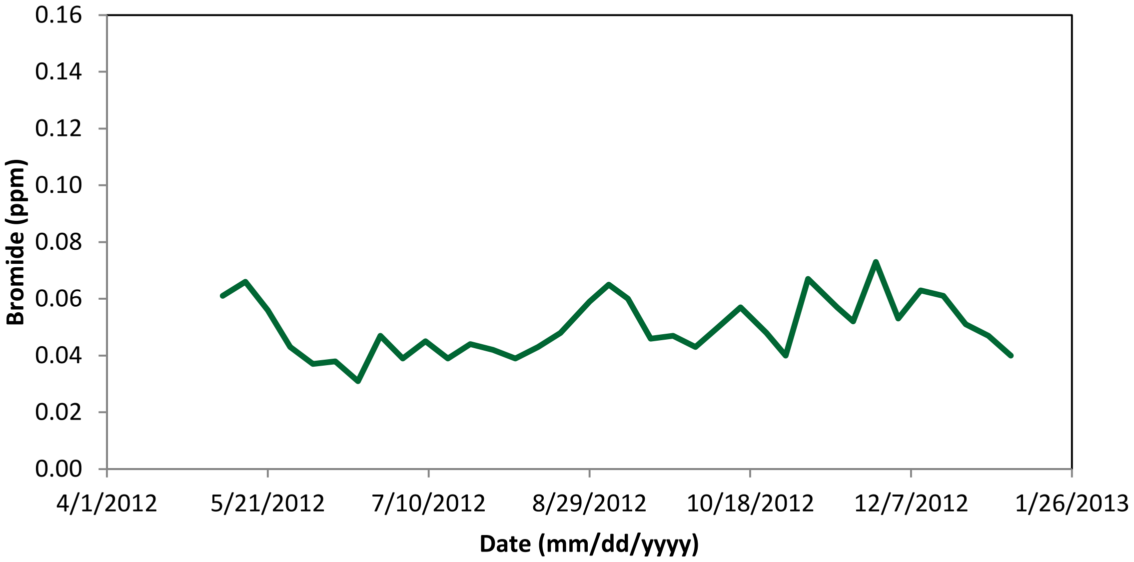

Figure 24: 2012 Red River bromide at Fargo influent (analysis by Fargo WTP)

5.1.3. Ozone Chamber Influent Bromide Concentrations

The concentration of bromide at the influent of the ozonation chamber is in Figure 25. Over the research sampling period, the bromide concentration found in the influent chamber of the ozone disinfection system had an average concentration of 0.09 ppm, a maximum of 0.15 ppm, and a minimum value of 0.04 ppm. The highest bromide concentrations occurred during the summer months between June and August (Figure 25). The higher concentrations of bromide stem from the groundwater sources used during those days for water treatment. Comparing Figure 25 and Figure 26, the times of increased well flow in the summer correspond to the times of high bromide concentration in the ozone chamber influent. In addition, the points placed on the graph in Figure 26 correspond to times of flow from the Moorhead Aquifer, the water source with the highest bromide concentration. During scenarios of decreased overall well flow higher bromide concentrations may still be maintained due to the use of the Moorhead Aquifer wells.

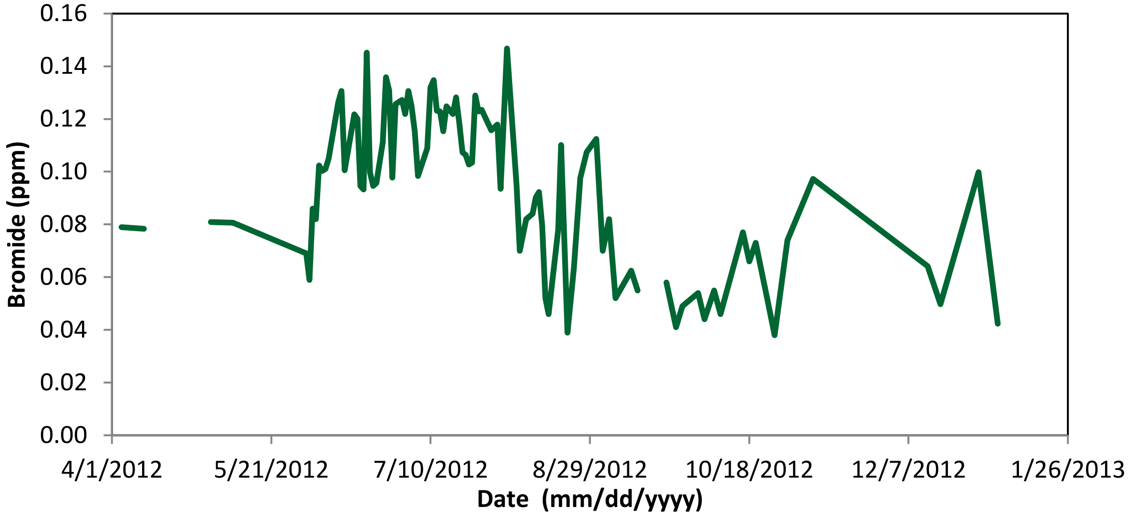

Figure 25: Ozone chamber influent bromide

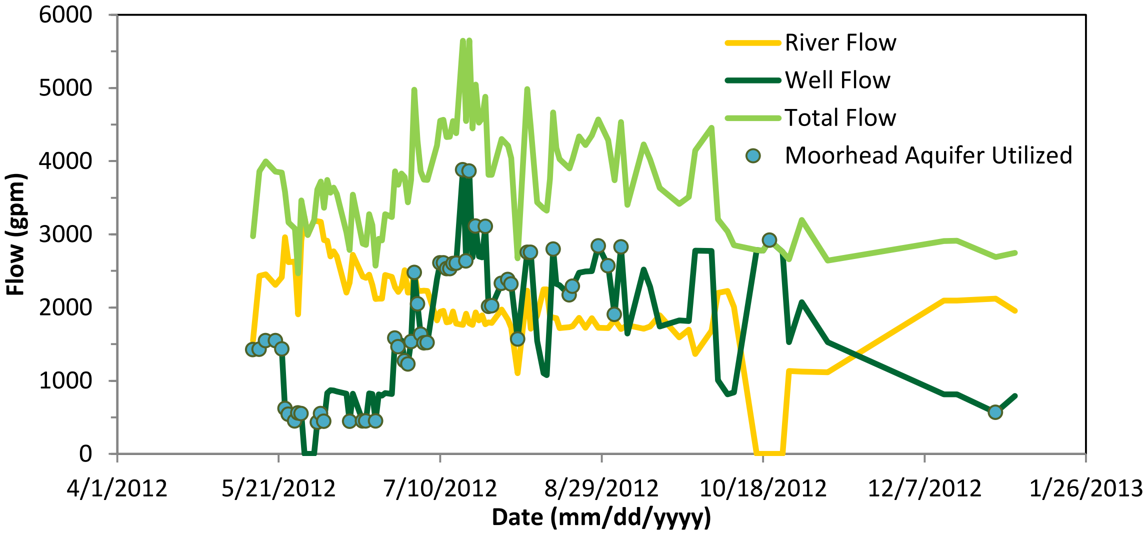

Figure 26: River, well, and total flow into Moorhead WTP

5.2. Bromate Concentrations in the Ozonation Chamber

Bromate concentrations were analyzed at the effluent points of each section in the ozone chamber: Section 1, Section 2, and Section 3. The bromate concentration results for each location are in Figures 27 and 28. Due to the continuous flow through the contact chambers, the bromate concentrations in Figure 27 are a cumulative value of the amount of bromate formed.

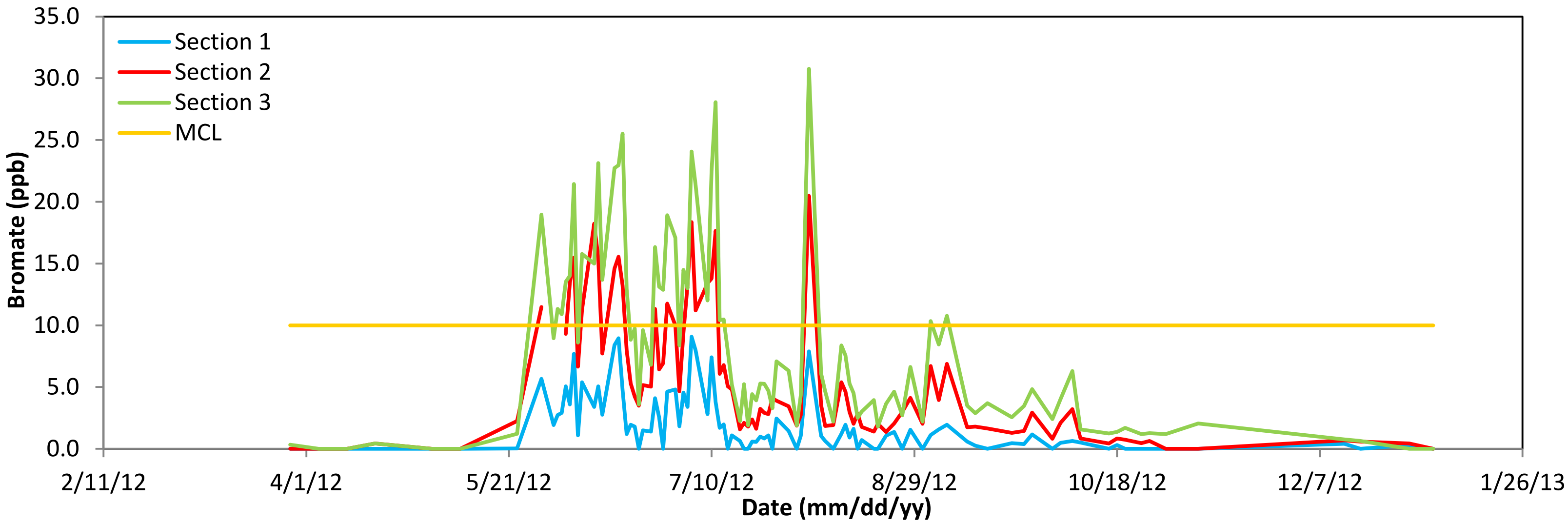

Figure 27: Cumulative bromate formation in ozone chamber sections

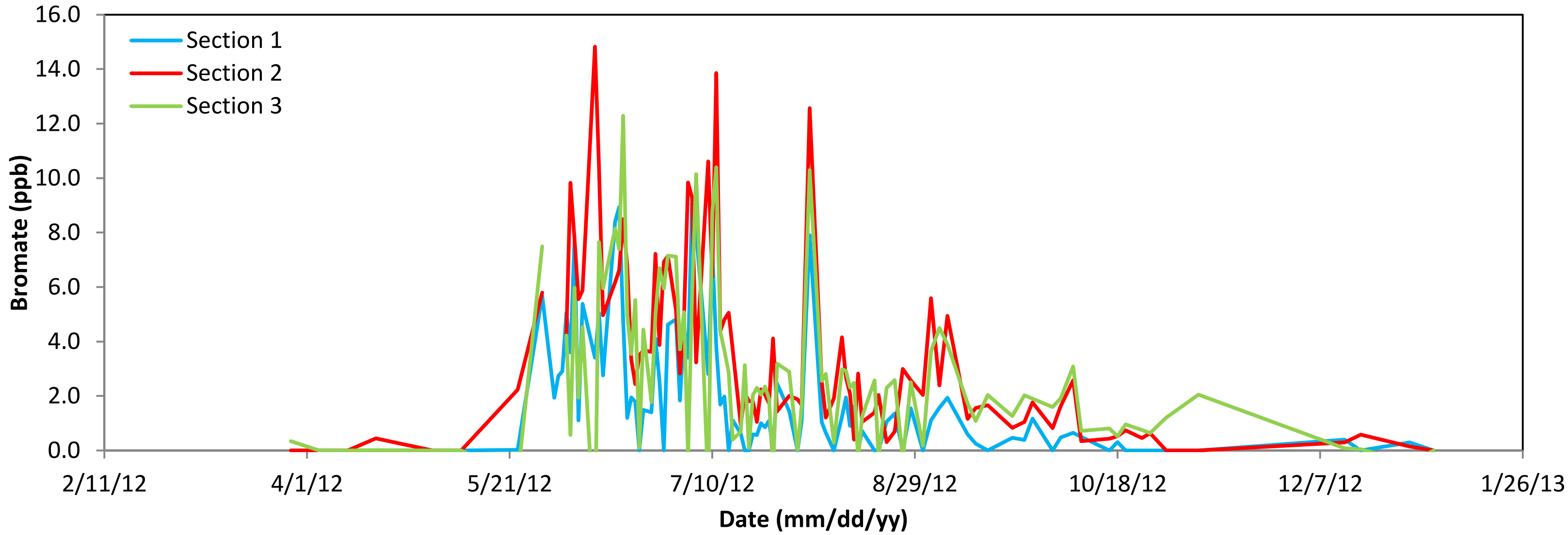

Figure 28: Individual bromate formation in ozone chamber sections

Bromate formation occurred in all three sections of the ozone disinfection chamber at the Moorhead WTP. The bromate formation varied throughout the sampling time but there were times when it exceeded the MCL, making it a valid concern to the treatment plant. The highest concentrations of bromate formed during the summer months, between the months of late May to early August. The bromate formation was also found to vary from day to day leading to the hypothesis that the amount of bromate formed is dependent on operational conditions at the treatment facility.

To examine the amount of bromate formed specifically in each section of the ozone chamber, the concentration found in the preceding location was subtracted from the concentration found in the following location. For example, to determine the amount of bromate formed specifically in Section 3 of the ozone chamber, the cumulative bromate found in Section 2 was subtracted from the cumulative bromate found in Section 3. Figure 28 shows the bromate formation formed individually in each section of the ozone chamber. From this figure it can be seen that a lesser amount of bromate is formed in Section 1 of the ozone chamber with more bromate forming in Sections 2 and 3. Comparing Section 2 and Section 3, both sections produced similar amounts of bromate, however, over the entire sampling period, Section 2 had the highest bromate formation of 14.8 ppb compared to 12.3 ppb and 9.1 ppb for the Section 3 and Section 1 respective maximums.

5.2.1. Bromine Mass Balance Analysis

As a form of analysis check, the ozone chamber effluent was analyzed for bromide concentration. By adding the bromide concentrations found in the ozone chamber effluent to the effluent bromate, the effluent bromine in the ozonation chamber was estimated. Effluent bromine should be approximately equal to the influent bromide under the assumption that the influent water to the ozone chamber is free of bromate. Figure 29 shows the influent bromide to the ozone chamber and the total bromine in the ozone chamber effluent.

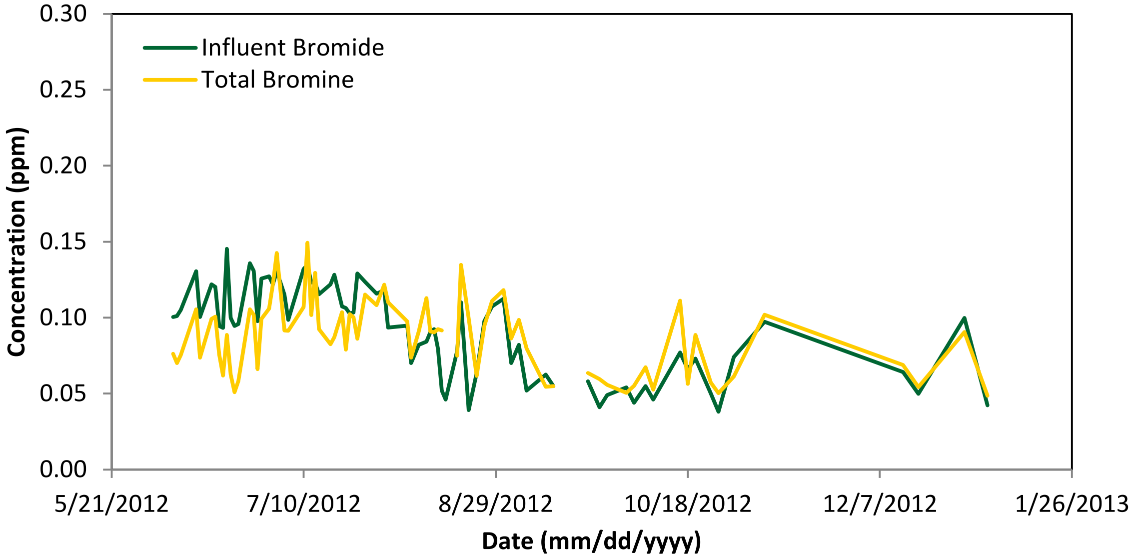

Figure 29: Total bromine in the ozone system used for analysis accuracy evaluation

By comparing the influent bromide and total bromine is Figure 29, the analysis was found to be less accurate during the times of high bromate formation, during the months of June to early August but improved and was more accurate during the later months of the sampling period. The difference between influent bromide and the calculated effluent bromine may be subject to a small percentage of error as other bromine species were not analyzed for this analysis. During incomplete oxidation, it is possible that other bromine species rather than bromide and bromate attributed to the overall total bromine. The difference in values found in Figure 29 averaged 0.018 ppm, a value less than the minimum detection limit of the IC equipment used for bromide analysis, providing that the bromide and bromate analysis for this research produced reasonable results.

5.3. Bromate Formation Influential Factors

Bromate formation is proportional to the initial bromide concentration in the water and ozone dose applied but it is influenced by other water quality parameters such as temperature, pH, and organic content. The effects of ammonia were not considered as ammonia additions were not conducted at the Moorhead WTP during the sampling period.

5.3.1. Influence of Temperature on Bromate Formation

During sample collection, the temperatures of the water samples were recorded resulting in the temperature graph in Figure 30. Sample temperatures did not vary by a significant amount during the treatment process. The sample temperatures found at the ozone chamber influent were almost equal to the temperatures found at the effluent of the ozone chamber so an average temperature was calculated and utilized for future analyses as the overall sample temperature (Figure 30).

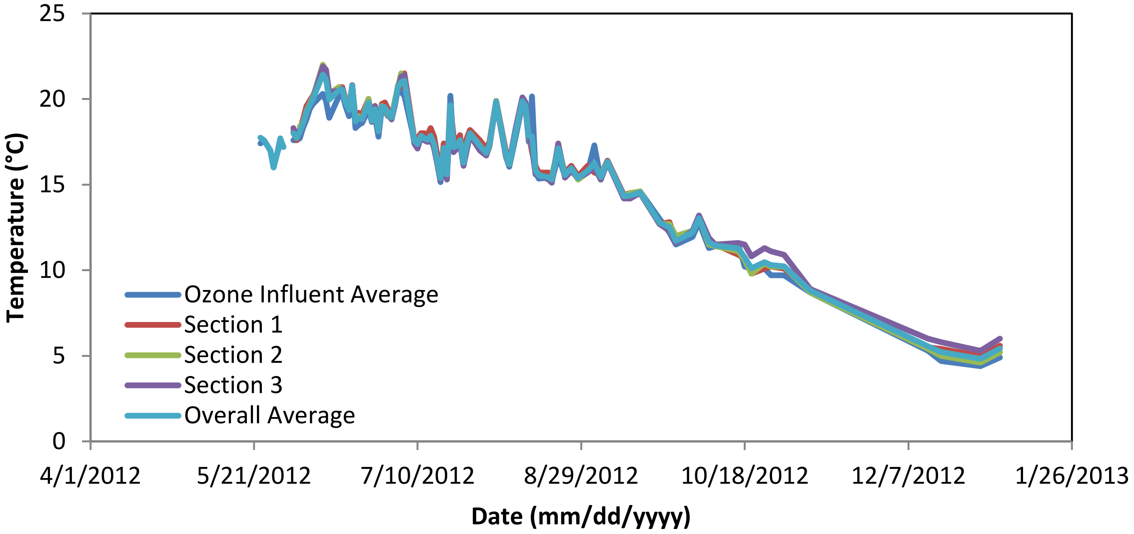

Figure 30: Temperatures of collected samples

It has been suggested through past literature that an increase in temperature correlates with an increase in bromate formation. To analyze the effects of temperature on bromate formation on a full-scale treatment system, the water temperature was compared to the total bromate formed for each sample collected at the Moorhead WTP (Figure 31). It was observed that the highest bromate formations occurred during the summer months of late May to early August, during the times of high temperature. The temperatures of the samples during the time of high bromate formation occurred at temperatures, in general, greater than or equal to approximately 16.5°C (Figure 31). As the sample temperature decreased below 16.5°C the bromate formation decreased and only exceeded the MCL twice (10.3 and 10.8 ppb) over the next five months of sampling. Sample temperatures were not available for those samples prior to 5/23/2012 so the recorded temperature of the finished water was used to estimate the water temperature within the ozonation chamber for the missing points. Further, using Figure 32 a trend can be observed between bromate formation and temperature. Increases in temperature correlated with increases in bromate formation. Using the MCL concentration as a guideline, the first concentration to surpass the MCL for bromate formation occurred at approximately 16.5°C. The temperature of 16.5°C is an approximation using the data available through this project. More data points are needed to determine the exact breakpoint temperature, however, 16.5°C provides a good estimation of the impact of temperature on bromate formation. In addition it was also observed that not all periods of high temperatures produced high bromate concentrations, meaning that temperature is an influential factor but does not dictate bromate formation under all conditions. Other parameters are also affecting the bromate formation process.

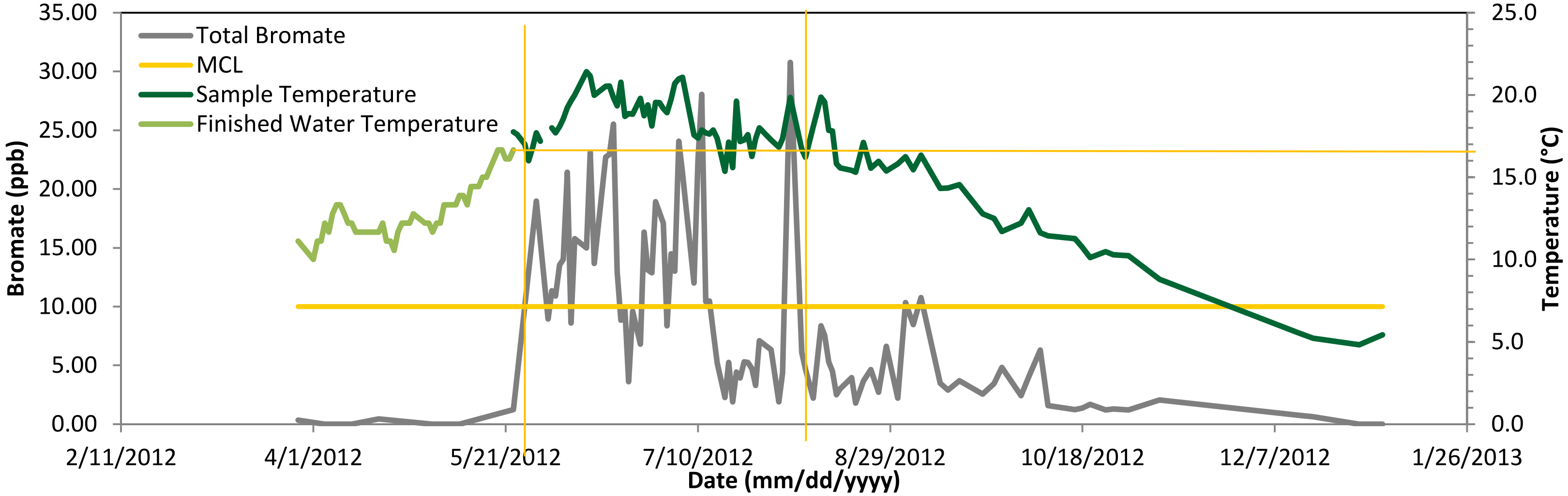

Figure 31: Temperature of collected samples influence on total bromate formation

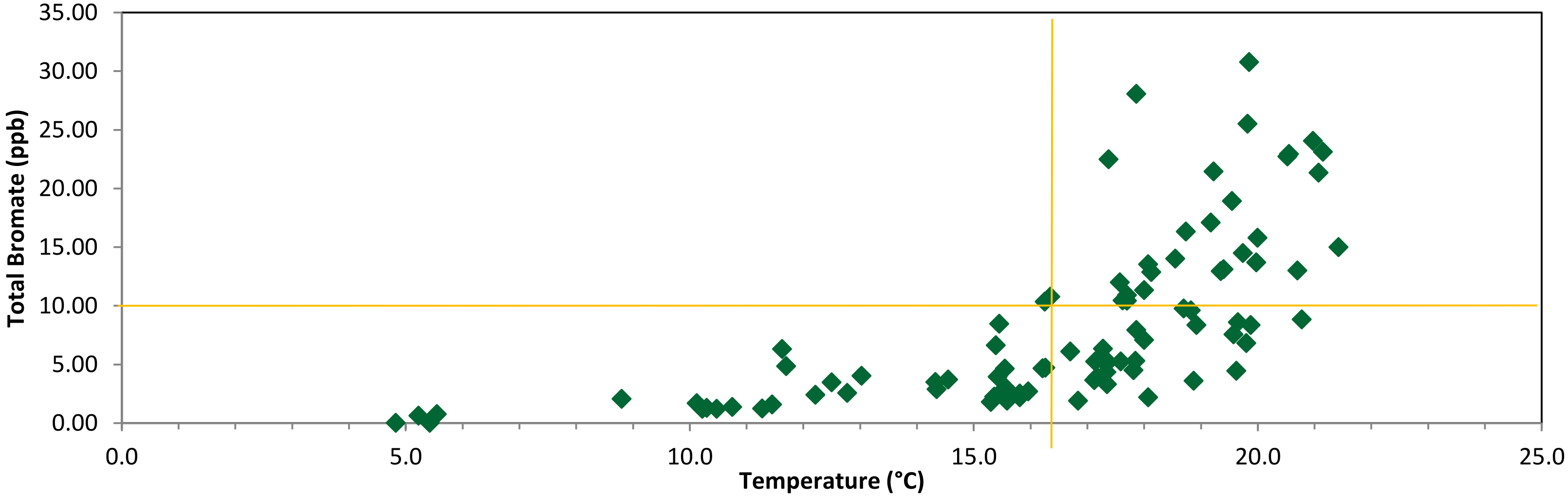

Figure 32: Total bromate concentration vs. temperature of collected samples

5.3.2. Influence of Bromide on Bromate Formation

The bromide concentration found in the ozonation chamber influent was compared to the ozonation chamber effluent bromate to determine the influence of bromide on bromate formation (Figure 33). The bromide concentration in the influent chamber to the ozone disinfection system was found to be highest during the summer months, likely due to the increase in well use at the Moorhead WTP. Through a comparison of the total bromate formed and the influent bromide in Figure 34, the highest bromate also formed during the time of increased bromide in late May to early August (Figure 33).

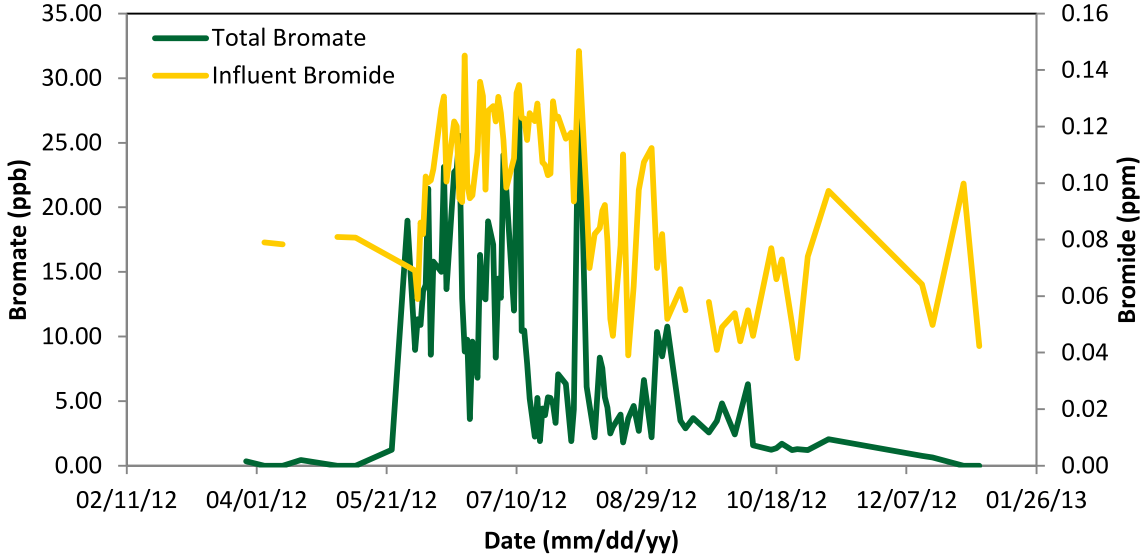

Figure 33: Ozone influent bromide and its influence on total bromate formation

There are sampling times of relatively high bromide concentrations that produced lower bromate concentrations (Figure 33), meaning there are other parameters are influencing the reaction of ozone and bromide. To determine the effect of temperature on bromate formation based on influent bromide, the samples were divided by temperature in Figure 34. Knowing that 16.5°C was found to be influential on bromate formation, it was applied to bromide's influence on bromate formation. At temperatures below 16.5°C, no correlation between bromide and bromate was observed. At temperatures above 16.5°C, a positive correlation was determined. Increases in bromate formation generally occurred with increases in bromide concentration in the influent. Because bromate is proportional to the bromide, there must be operational conditions in the treatment process that are reducing the formation of bromate during these times of high bromide concentrations.

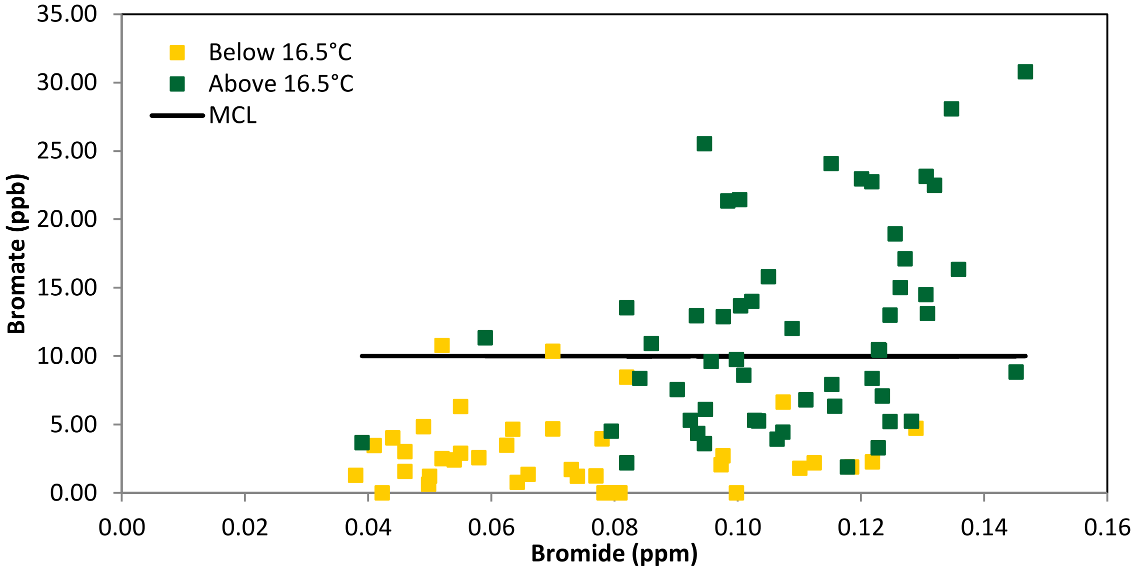

Figure 34: Total effluent bromate vs. ozone chamber influent bromide at different temperatures

5.3.3. Influence of Ozone Dose on Bromate Formation

The applied ozone dose was recorded at time of sampling and was used in Figure 35 to compare the ozone dose to the effluent bromate concentration. During the sampling period, variations in applied ozone dose were observed and ranged from 1.5 to 7.1 mg/L. Changes in ozone dose at the Moorhead WTP are conducted to meet CT requirements for disinfection. Changes in water temperature, pH, and organic content can all impact ozone demand and result in necessary changes in ozone dose to obtain an appropriate ozone residual for disinfection credits.

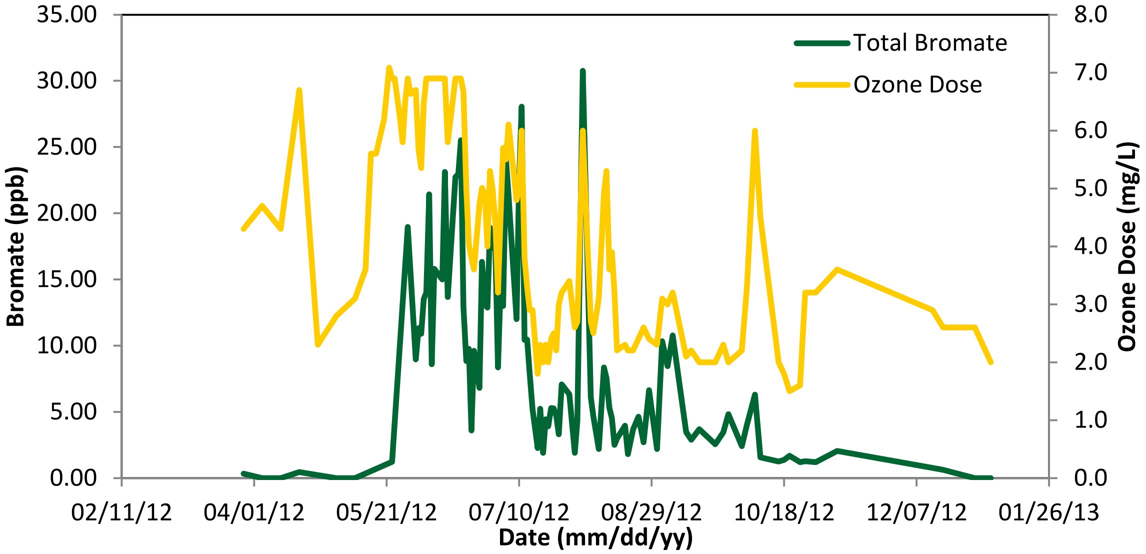

Figure 35: Ozone dose influence on bromate formation

As the ozone dose was not always an indication of increases in bromate formation for all samples analyzed and times of high ozone doses in the fall produced relatively low concentrations of bromate, temperature was thought to play a role in the relationship between ozone and bromate formation. In Figure 36, the samples were split between those occurring at temperatures greater than and less than 16.5°C. A strong positive trend, but weak correlation between ozone dose and bromate formation was observed. The samples collected at temperatures below 16.5°C corresponded to low bromate formation for a range of ozone doses between 1.5 mg/L to about 7.0 mg/L. However, at temperatures greater than 16.5°C, increases in ozone dose corresponded to increases in bromate formation at a similar range of applied ozone doses. It can be concluded that although the ozone dose is a predominant influential factor in bromate formation, its affect on bromate formation in a full-scale system is affected by seasonal changes in the water temperature.

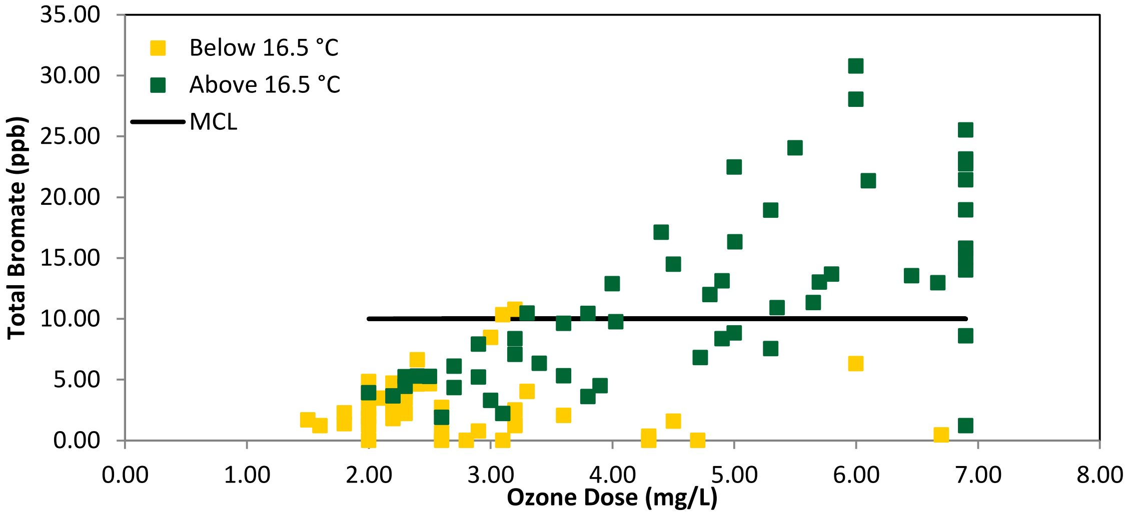

Figure 36: Total bromate vs. ozone dose

5.3.4. Influence of pH on Bromate Formation

The pH was analyzed at each section of the ozonation chamber and compared to the total bromate formation to analyze the influence of pH on bromate formation at the Moorhead WTP (Figure 37). Through the sampling period it was observed that the pH was relatively stable throughout the ozonation chamber during the summer months. When the point of recarbonation was changed on 9/25/2012 from Cell A to Cell C, the pH within the ozonation chamber began to vary between sections. Section 1 pH remained high while Sections 2 and 3 pH values were decreased (Figure 37).

Using Figure 37, no strong relationships between pH and bromate formation become apparent. Looking at Section 1 of the ozone chamber individually, and separating the samples by temperature (Figure 38) the role of pH and its influence on bromate formation at the Moorhead WTP is better understood. At low temperatures, the bromate formation was minimal at pH values ranging from about 9.0 to 11.5 and no trend was observed. At high temperatures, the bromate formation was variable between a pH of 8.75 to 9.75 and again no trend was observed.

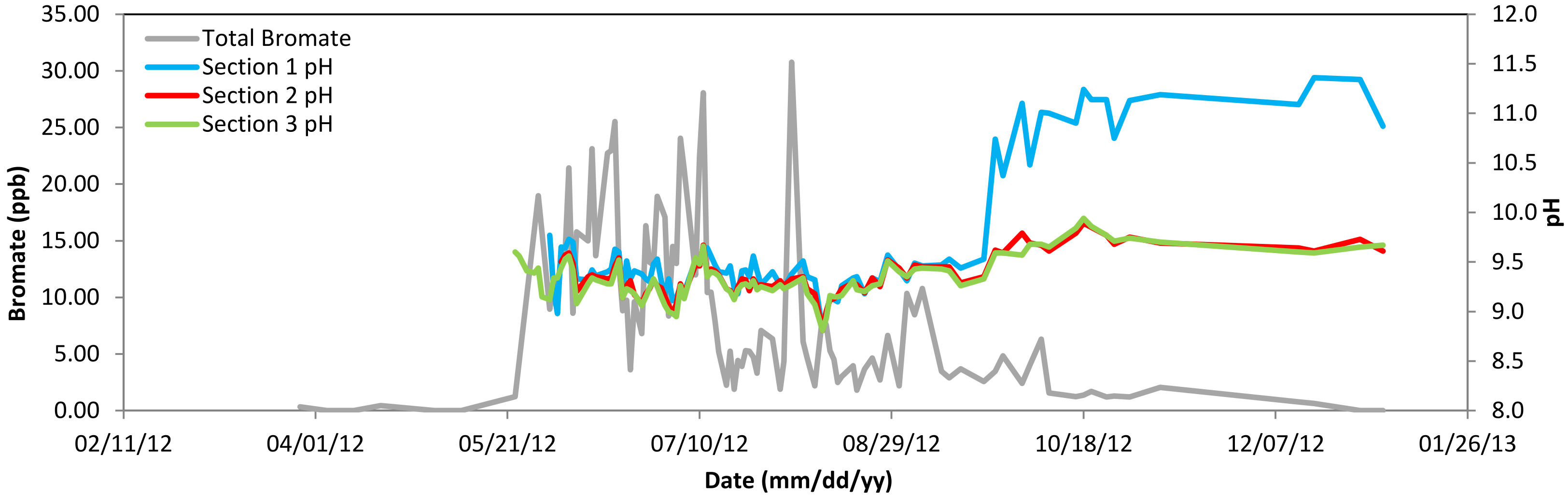

Figure 37: pH influence on total bromate formation

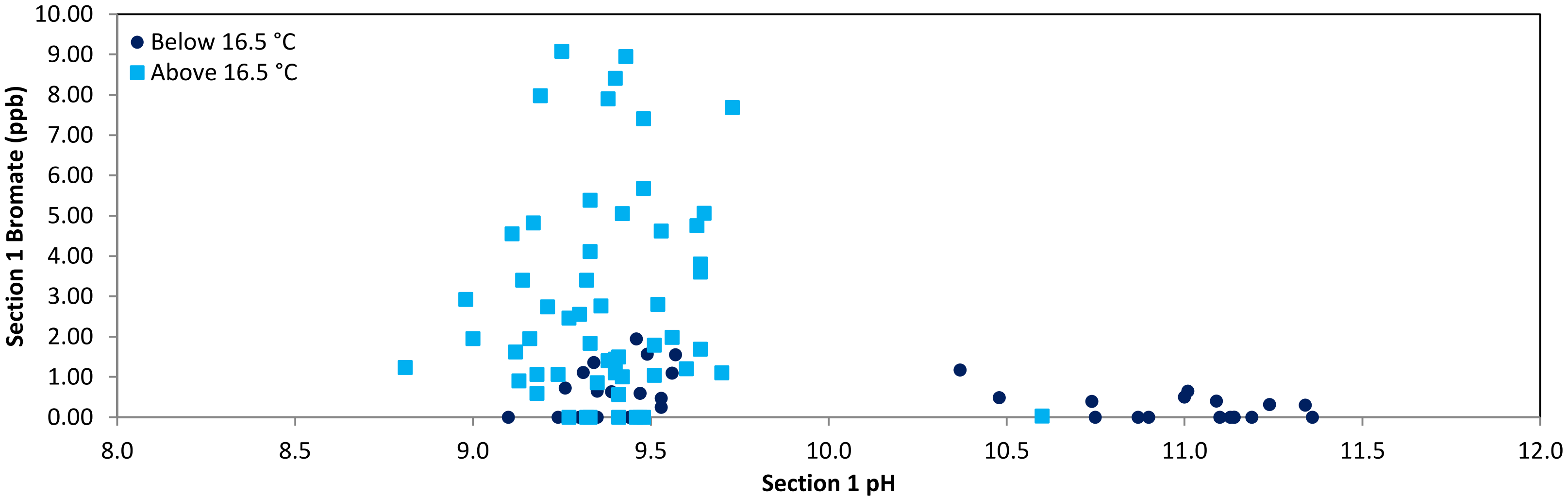

Figure 38: Section 1 bromate vs. Section 1 pH

Under a similar analysis as was conducted for the pH in Section 1, the pH in Section 2 can be analyzed at different temperatures (Figure 39). At temperatures less than 16.5°C bromate formation was minimal at pH values ranging from 9.1 to 9.9. No trend was observed between Section 2 bromate formation and Section 2 pH at the low temperature range. However, at temperatures greater than 16.5°C, a positive trend but poor correlation is observed. For a range of pH values between 8.8 to 9.7 a general positive trend occurred between increases in pH and increases in bromate formation (Figure 39).

Similar results were found through the Section 3 analysis for the influence of pH on bromate formation. By splitting the samples by temperature in Figure 40 two relationships were formed. At the lower temperature range, those temperatures below 16.5°C, the bromate formation was again minimal at pH values from 9.1 to almost 10.0. At the higher temperatures, above 16.5°C, a positive trend was observed. At pH values ranging from 8.8 to 9.7, a general positive trend was found between increasing pH and increases in bromate formation (Figure 40).

Conclusions about the influence of pH on bromate formation were made through the comparison of individual section pH and section bromate. At the Moorhead WTP, the influence of pH on bromate formation is dependent on the ozonation chamber section and temperature.

At all temperatures and pH ranges in Section 1, no trend was observed between changes in pH and bromate formation. Sections 2 and 3 pH were found to positively influence bromate formation at temperatures greater than 16.5°C. At temperatures less than 16.5°C the pH found in Sections 2 and 3 were not observed to influence bromate formation.

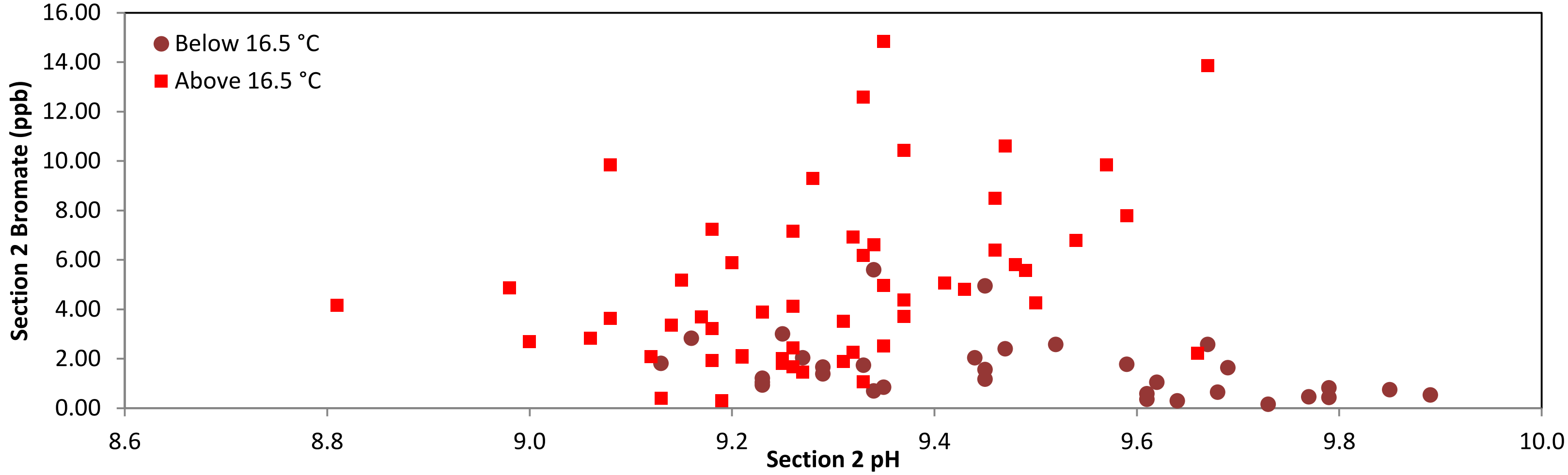

Figure 39: Section 2 bromate vs. Section 2 pH

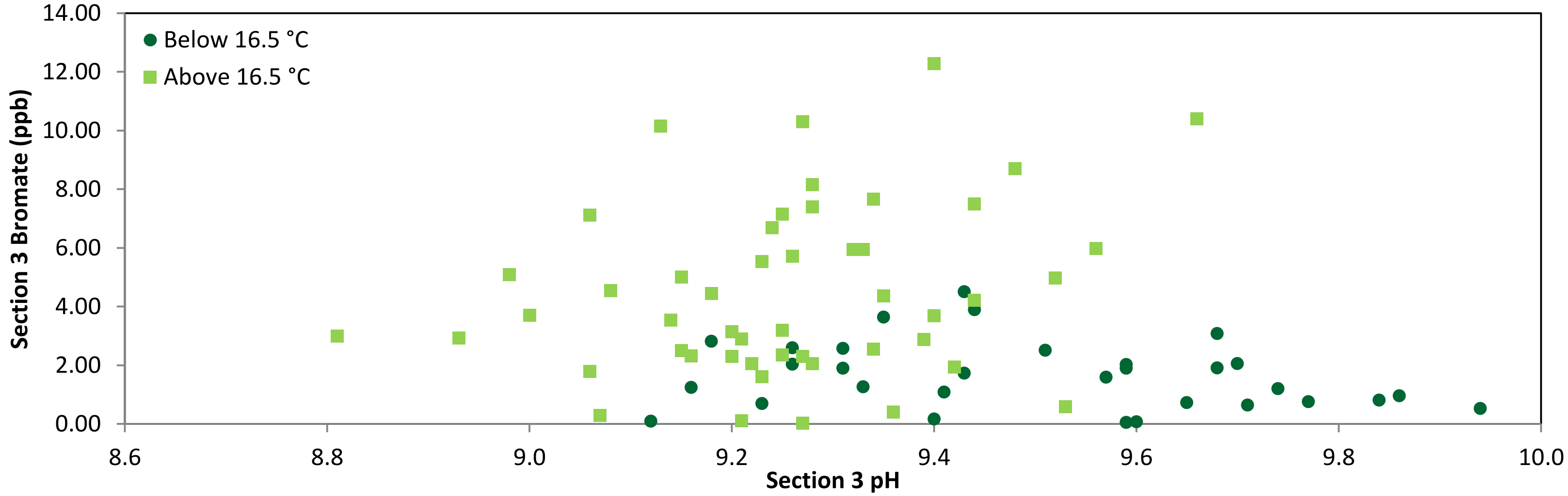

Figure 40: Section 3 bromate vs. Section 3 pH

The difference in influence of pH on bromate formation between the different sections of the ozonation chamber may be attributed to the organic content between the sections. Section 1 is used for organic reduction and therefore contains higher concentrations of organics that does Sections 2 and 3 possibly causing an interference with bromate formation.

5.3.5. Influence of Organic Content on Bromate Formation

The TOC at the ozonation chamber influent was recorded and compared to the effluent bromate formation in Figure 41. Influent TOC was variable throughout the sampling period and ranged from 1.0 to 5.0 mg/L. Variations in TOC can be attributed to changes in the source waters. Spikes in TOC data often are a response to rain events that cause overland runoff to wash particulates into the river. Gradual increases in TOC in the spring can be attributed to spring snowmelt increasing the TOC found in the Red River or due to upstream discharges to make room for flood water storage. In the summer months, gradual decreases in TOC at the influent to the ozonation chamber are a result of influent mixing of the lower TOC groundwater with the higher TOC surface water.

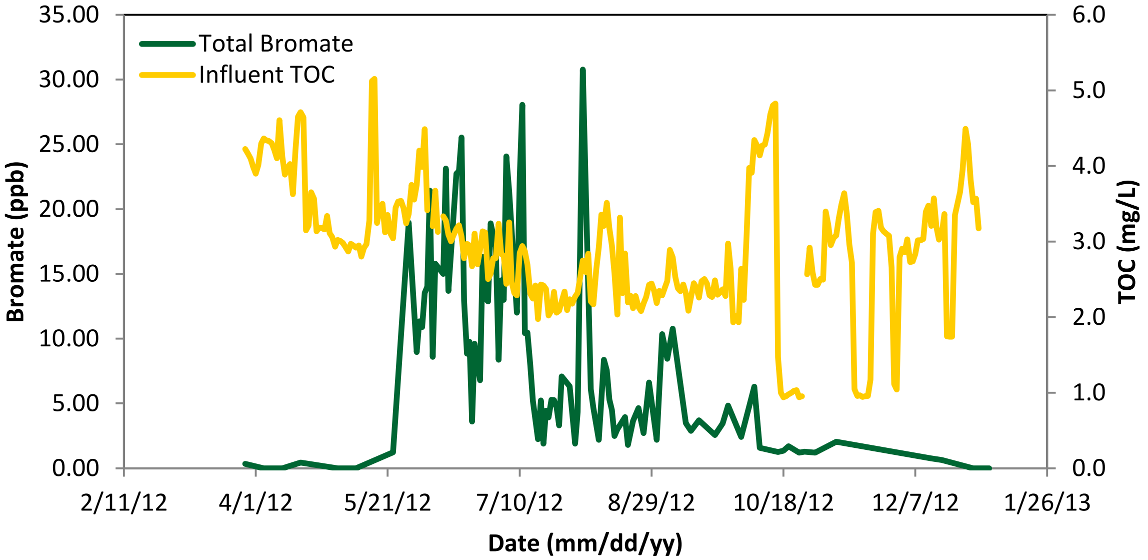

Figure 41: Influence of influent TOC to ozonation chamber on bromate formation

The TOC concentration in the influent water to the ozone disinfection chamber and total bromate formed are plotted together to study the potential impact of TOC on bromate formation (Figure 41). It was observed that a general decrease in influent TOC occurred during the months of high bromate formation but no strong correlation was determined through the use of Figure 41.

By splitting the samples by temperature, those less than 16.5°C and those greater than 16.5°C a better trend is observed (Figure 42). At the lower temperature range, bromate was found to be minimal, less than or almost equal to the MCL, during different TOC concentrations ranging from near 1.0 mg/L to approximately 5.0 mg/L. At the higher temperature range, bromate formation exceeded the MCL more often but no distinguishable trend was observed between changes in TOC in the influent water to the ozonation chamber and the resulting effluent bromate.

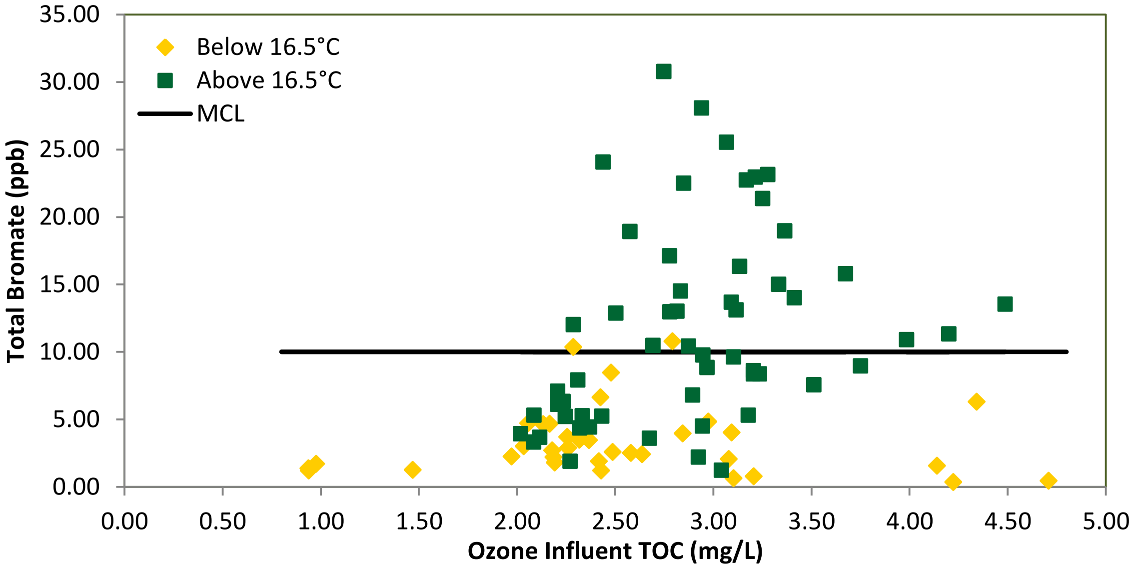

Figure 42: Bromate vs. ozonation chamber influent TOC

At the Moorhead WTP the organic breakdown process is unique. The first section of the ozone contact chamber is used specifically for the breakdown of organics through the use of high pH from the softening process (Chapter 3). Through the use of ozone, a strong oxidant, organic reduction is possible and is used for taste and odor control. Ozone breaks down cyclic organics, into less aromatic chain organics. Through the initial TOC analysis, reduction in TOC was limited and it was calculated that on average over the sampling period was only reduced by 5% through the ozone disinfection system. Unfortunately, a TOC analysis measures the total amount of organics not the change in organic form. To better understand the bromate formation due to organics, UV254 was measured as it better describes the breakdown of the taste and odor compounds found in the water.

UV254 analysis was conducted from mid August to January and the results are shown in Figure 43. The greatest variations in UV254 between sampling days occurred during dramatic flow changes, such as the removal of all river flow from 10/16/2012 to 10/24/2012 as shown in Figure 43.

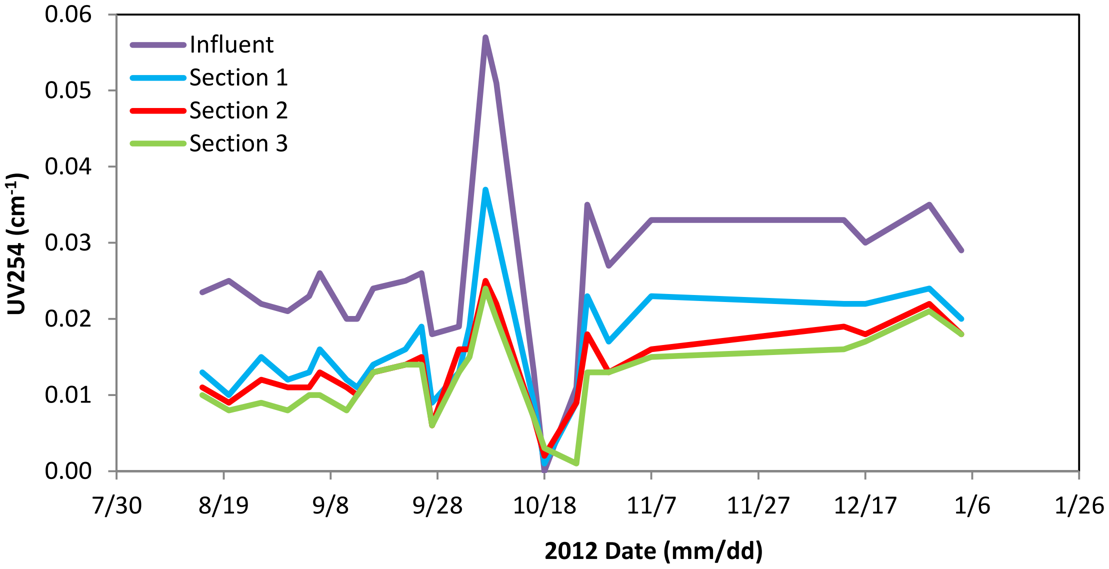

Figure 43: UV254 throughout ozonation chamber

The greatest reductions in UV254 within the ozonation chamber appear to occur between the influent and Section 1 of the ozone contact chamber (Figure 43). Through percent reduction calculations it was determined that Section 1 removed on average 37% of the organics as compared to 17% and 12% from Section 2 and Section 3 respectively (Figure 44). It was also observed that during the months of August and September, the UV254 reduction in Section 1 was greater than in the later months. Considering those samples in Figure 43 collected before 9/28/2012, the UV254 percent reduction in Section 1 was 42% with Sections 2 and 3 removing less at 15% and 12% respectively. As the water temperature further decreased into the months of October through the end of the sampling period, the percent reduction of UV254 also decreased and on average was 34%, 16%, and 9% for Sections 1, 2, and 3 respectively.

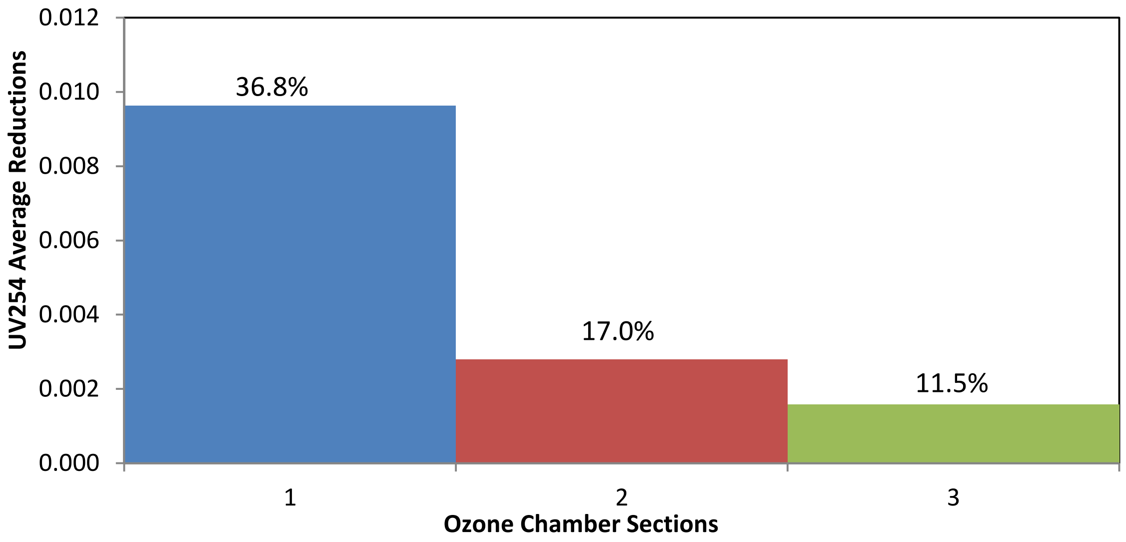

Figure 44: Average UV254 reductions in the ozonation chamber

The UV254 average reductions in absorbance units are shown in Figure 44. The greatest UV254 reductions did occur in the first section of the ozone contact chamber. The values shown in Figure 44 are the average removal over the sampling period for each section of the ozonation chamber. If Figure 28 is recalled, it was found that Section 1 of the ozone contact chamber produced the least amount of bromate as compared to Sections 2 and 3. Sections 2 and 3 produced similar amounts of bromate. It may be suggested that the UV254 reduction in the first section reduces the bromate formation. The ozone is utilized for the organic reduction, resulting in less ozone available for bromide oxidation to bromate. As the organic content is reduced in Section 1 and the water passes into Section 2, the ozone is no longer consumed by organic matter and is available for bromide oxidation to bromate, increasing bromate formation.

The organic content available in the first section also helps to explain why the first section of the ozone chamber behaved differently concerning pH and bromate formation. It was concluded that the pH in the first section of the ozonation chamber did not influence the bromate formation at all temperatures but was influential in Sections 2 and 3 at high temperatures. The organic content in Section 1 of the ozonation chamber inhibits bromate formation through ozone and hydroxyl radical scavenging and reduces the influence of other bromate formation parameters.

5.3.6. Summary of Bromate Formation Influential Parameters

Through the comparison of water quality parameters, such as pH, temperature, and organics along with operational settings such as ozone dose, bromide concentration, and source water flow, qualitative influences on bromate formation were made. This research was conducted on a full-scale water treatment system, making it difficult to apply controls to the system. Seasonal changes in the source water lead to changes in the bromate influential parameters. Without the ability to apply controls during the research sampling period, quantitative relationships between bromate formation and influential parameters were not determined. However, qualitatively, it was determined that increases in bromate formation are caused by increases in temperature, pH, bromide, and ozone dose, while decreases in bromate formation are caused by increases in organics. It was determined that the influential parameters are interrelated as the parameters interact with each other causing indirect changes in bromate formation. Specifically, it was observed that the bromate influential parameters were temperature dependent. pH, bromide, and ozone dose were more influential to bromate formation at those temperatures greater than 16.5°C. Due to the seasonal changes in water quality and bromate formation, an analysis on the changes in operation is necessary.

5.3.7. Influence of Operational Controls on Bromate Formation

To better understand the bromate formation at the Moorhead WTP, an investigation into the highest bromate formation during the sampling period was conducted. On August 3rd, 2012, the ozone chamber effluent bromate concentration was 30.8 ppb. Looking more closely at the sample taken on this date a greater understanding for bromate formation is made. For example, on August 3rd, 2012 there was a rain event that occurred during a very dry season. After the rain event, increases in river total, non-carbonate, and calcium hardness (Figure 45) as well as increases in TOC (Figure 46) occurred due to the overland runoff. The changes in water quality of the Red River created difficulties in the treatment process.

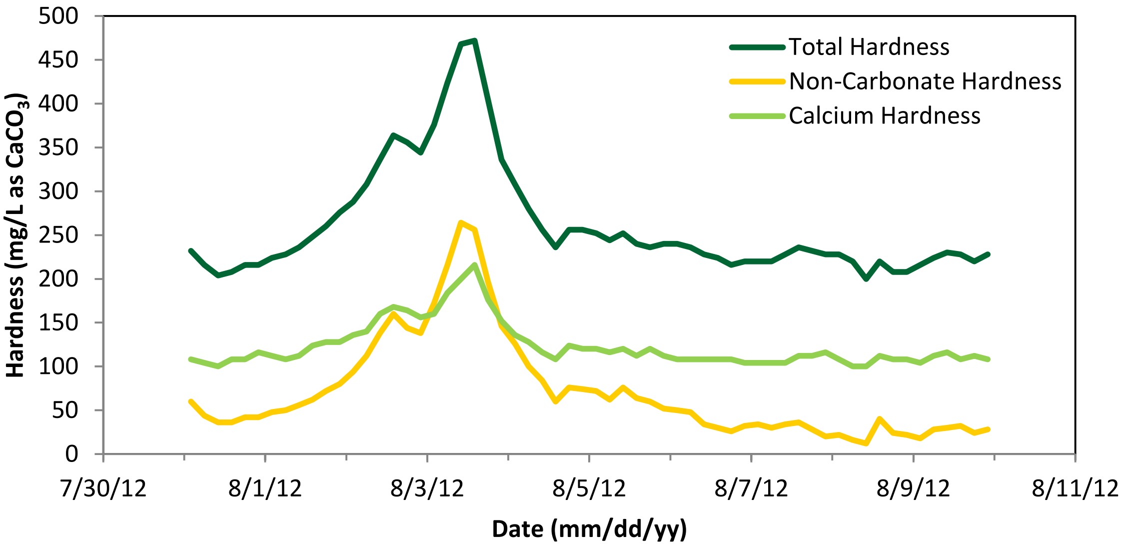

Figure 45: Red River hardness during bromate spike

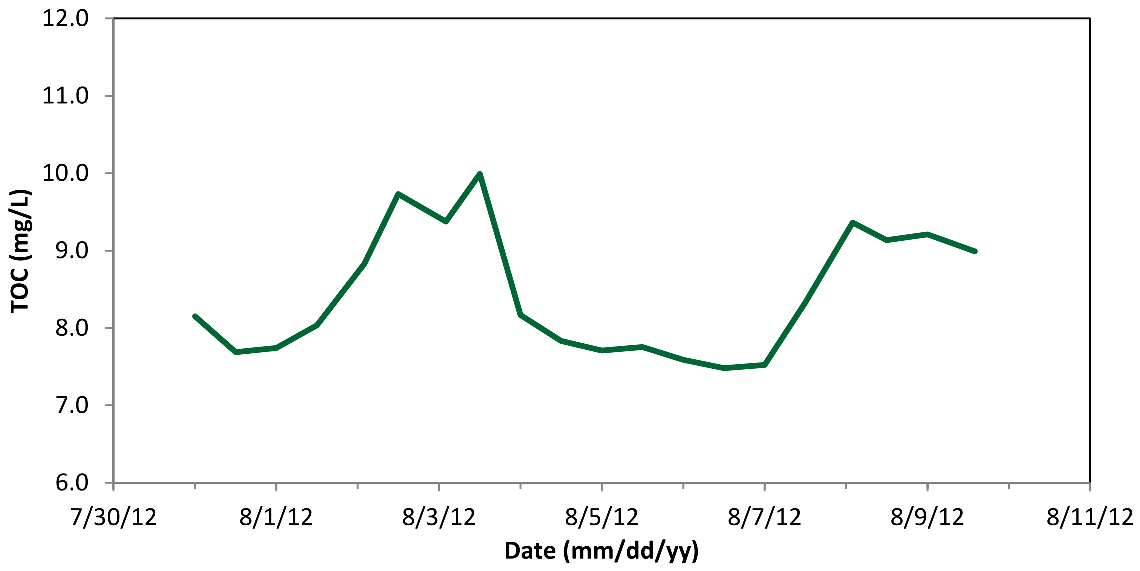

Figure 46: Red River TOC during bromate spike

During rain events, especially those after a dry period, the Moorhead WTP operators have a few methods to prevent changes in produced water quality due to the changes in the river quality. When the Red River hardness increases quickly, the WTP operators have a difficult time meeting hardness requirements in the softening basin. To meet hardness requirements, either more chemicals or a different blend of influent water is needed. To combat the changes in organics in the Red River, a water plant operator can again add more chemicals through the use of more coagulants or ozone, can change the source water, or can lower the pH to reduce ozone consumption. As the change in source water blending helps with both changes in hardness and organics, it is often used by operators. Changes in source water include adding well flow to decrease the needed river flow. In the meantime, while the change in source water blending takes effect increases in ozone dose are necessary to help with the increase in organics. In the event an operator is apprehensive about losing CT for disinfection, he or she even may lower the pH of the water to reduce ozone consumption. Changes such as these, however, also can produce other problems like bromate.

On August 3rd, 2012, changes such as those discussed were implemented to assist with the change in Red River water quality. On August 3rd, both the river and well water flow were decreased to the influent of the WTP (Figure 47). Due to the rain event, it is likely that the overall water demand decreased providing for the subsequent decrease in flow to the WTP. However, specifically, well 6B and 9 were utilized during this decrease in flow.

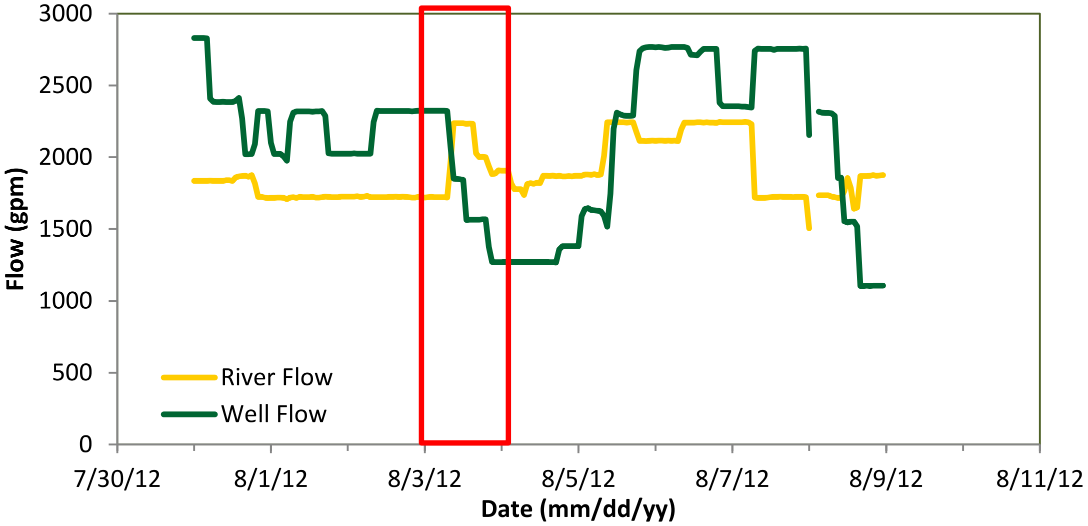

Figure 47: River and well flow into the Moorhead WTP during the bromate spike

As discussed previously, well 6B stems from the Moorhead Aquifer and is low in hardness relative to the other water source options. It is likely that this well was utilized to decrease the overall hardness of the influent water by blending with the increasing hardness in the river water. As this occurred the influent bromide concentration to the ozone chamber, shown in Figure 48, also increased. Prior to this study, the bromide concentration in the well options was not known. Through this study, it was determined that the Moorhead Aquifer contains the highest bromide concentration of the source water options. Without knowing the bromide concentrations in the well, the operators were introducing a much higher concentration of bromide into the ozonation chamber. Although, the addition of wells was a good way to reduce taste and odor issues and chemical doses it lead to other problems.

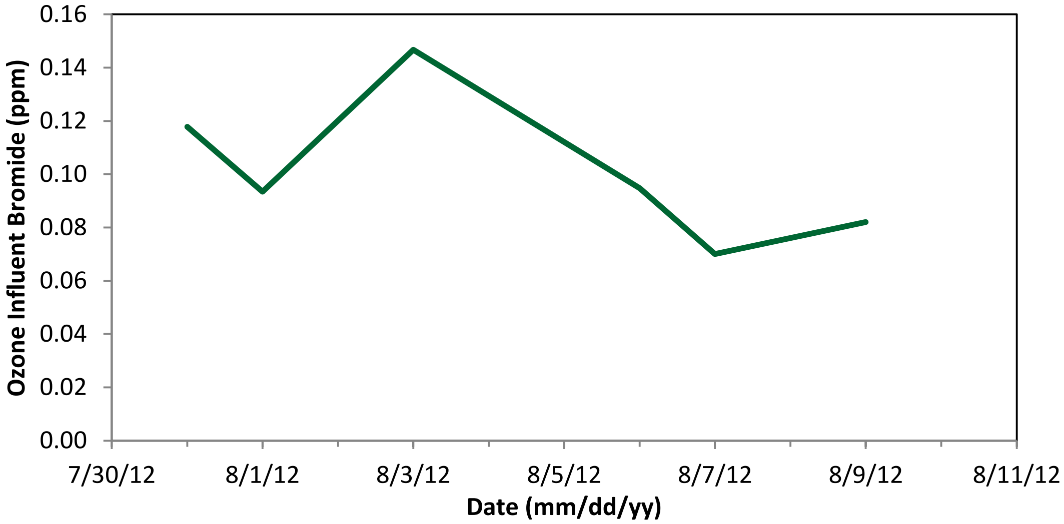

Figure 48: Ozonation chamber influent bromide concentration during bromate spike

As the river quality became worse, the ozone dose was increased throughout the day on August 3rd to prepare for the increase in TOC in the Red River from the rain event. As the influent TOC to the ozone system increased, operators continued to increase the ozone dose to 6.0 mg/L to meet the CT requirements (Figure 49). The ozone dose applied on August 3rd as compared to the days before and after the bromate spike on August 3rd are in Figure 49. The ozone dose was 2 to 3 mg/L higher on August 3rd.

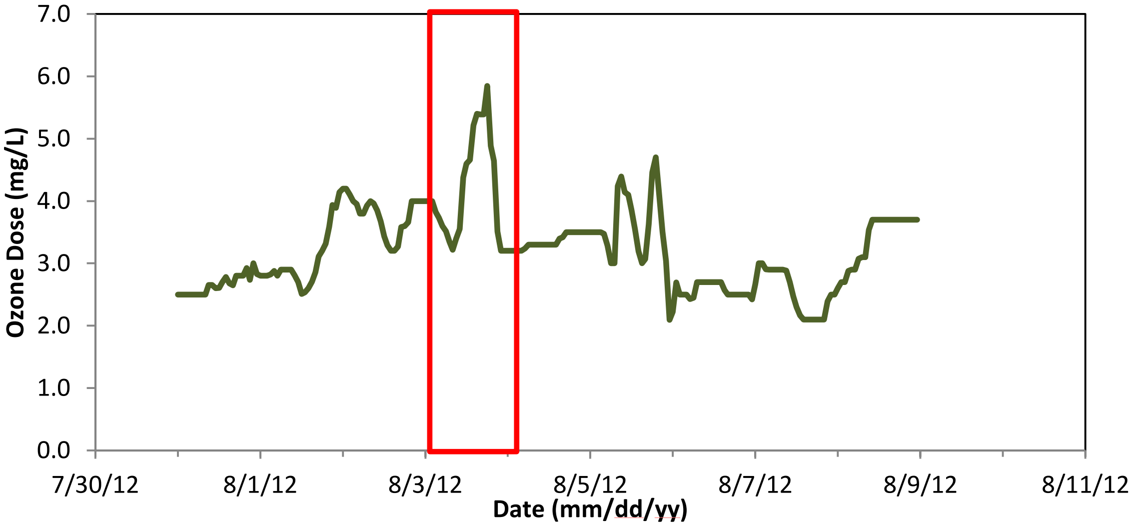

Figure 49: Ozone dose during bromate spike

Ultimately, the ozone dose is adjusted to meet CT requirements for disinfection. The CT at the Moorhead WTP during the days leading up to and following the bromate spike is shown in Figure 50. It was observed that on August 3rd, the CT decreased rapidly towards the minimum requirement for disinfection and then spiked to a CT almost 4.5 times higher than the required CT (Figure 50). The initial drop in CT is due to the fast increase in TOC in the river and the subsequent spike in CT immediately following is likely an overcompensation from the changes in source water flow and ozone dose increase. As the well water blended into the treatment process, the ozone chamber was producing a greater than necessary CT causing the quick increase in CT ratio, halting the drop in CT. The excess residual ozone now was available for further bromide oxidation to bromate.

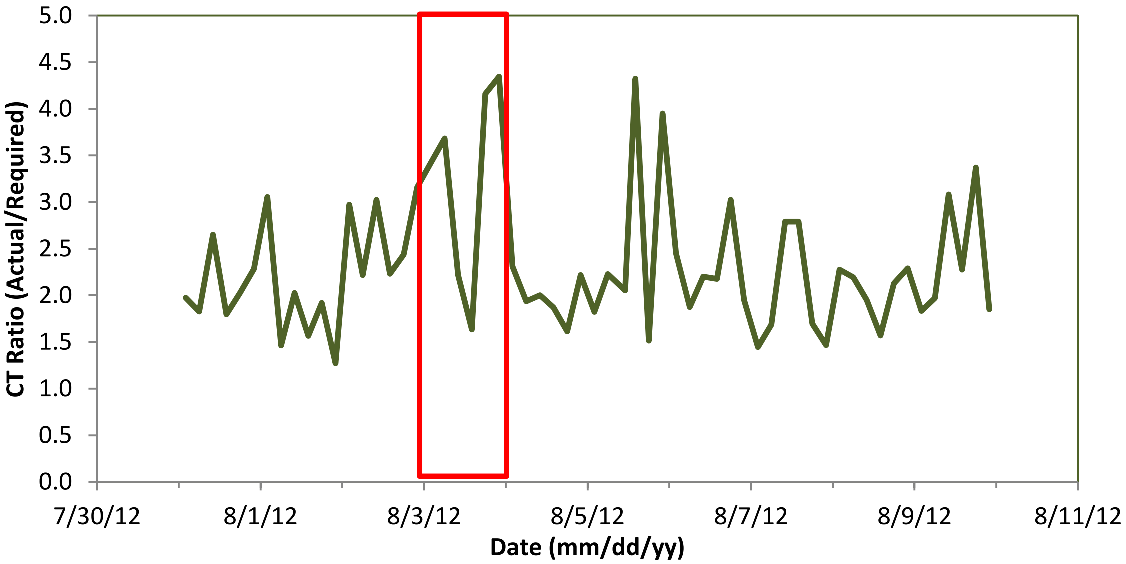

Figure 50: CT ratio during bromate spike

In addition to a higher ozone dose being applied to a higher bromide concentration, the pH of the water was also high. The pH of the water within the ozonation chamber is in Figure 51 for the days surrounding the bromate spike on August 3rd. It was observed that the pH was higher on August 3rd than the pH of the water in the ozonation chamber during some of the samples before and after the bromate spike. A lower pH in the ozonation chamber during the increase in organics may have increased the residual ozone and allowed the ozone dose to be lowered and in effect lowered the effluent bromate concentration.

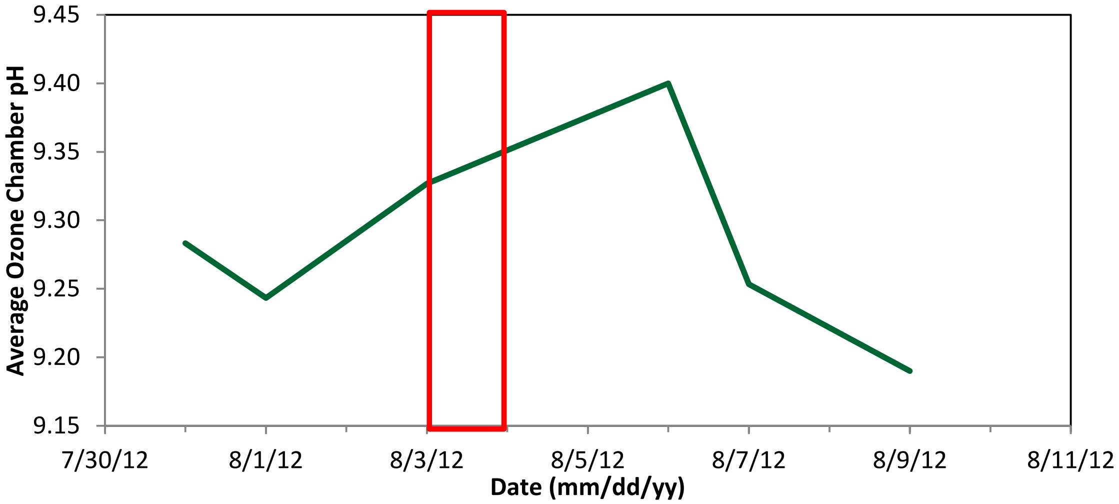

Figure 51: Water pH during bromate spike

Through the in-depth analysis on the bromate spike that occurred on August 3rd, it was determined that the operational controls of a WTP can influence bromate formation. It was shown that operators can influence bromate through changes in source water selection, ozone dose, and pH adjustments. Strategies for bromate minimization can be developed to implement more efficient changes in controls that meet both disinfection and taste and odor requirements while still minimizing bromate formation.

CHAPTER 6. BROMATE PREDICTION MODELING

As discussed in Chapter 5, much was discovered between the relationships of water quality parameters, operational controls, and bromate formation. However, due to the full-scale size of this research effort, determining quantitative comparisons becomes difficult. During the operation of a functioning WTP, many parameters change at one time making it difficult for researchers and operators to fully understand bromate formation. To assist the Moorhead WTP in optimizing their disinfection system to minimize bromate formation, a bromate prediction model was developed. Development was completed through a review of past literature, refinement through multiple regression analysis, and adjustments to meet Moorhead WTP requirements.

6.1. Review of Past Bromate Prediction Models

The prediction of DBPs has been studied for many years to assist treatment facilities in monitoring and limiting their formations. In a review conducted by Chowdhury et al. (2009), more than 48 existing publications have reported at least 118 models that were based on DBP prediction since 1983. Of these 118 models, 5 reports focused on bromate formation models (Chowdhury et al., 2009). The main types of models developed thus far for bromate formation are kinetic, artificial neural networks, and regression based. The regression based model was selected as an appropriate model for adoption by the Moorhead WTP because it is a similar type of model that the WTP is already utilizing for prediction of other water quality parameters within their facility. The basic equation for a regression model is as follows:

$$Y = e^{\beta_0} \times {x_1}^{\beta_1} \times {x_2}^{\beta_1} \dots {x_n}^{\beta_n} \tag{9}$$

The variables, x, generally are used to describe bromate influential parameters and the parameters, the β exponents, are used to provide a value as to how influential the variable is to bromate formation. Also, negative or positive β values dictate whether the influential parameter has a positive or negative correlation with bromate formation.

Through a review of regression models utilized for bromate prediction, it was observed that each model considered different influential parameters and each parameter, β, varied. The influential parameters included in the bromate prediction models are included in Table 12. The variation found in the model values suggests that different water sources behave differently during bromate formation, requiring each model to be fit to the influent water source and subsequent bromate formation parameters (Jarvis et al, 2007).

Table 12: Bromate influential parameters used in prediction models

Authors	Influential Parameters
Ozekin (1994)	pH, Br^-, ozone dose, DOC, time
Siddiqui et al. (1994)	pH, Br^-, ozone dose, DOC, time
Song et al. (1996a)	pH, Br^-, ozone dose, DOC, NH_3-N, IC, time
Sohn et al. (2004)	pH, Br^-, ozone dose, UVA, time, alkalinity
Tyrovola (2005)	pH, Br^-, ozone dose, time
Jarvis et al. (2007)	pH, Br^-, ozone dose, IC, NH_3-N, DOC, time
Lu, Krasner, and Liang (2011)	pH, Br^-, ozone dose, UV, temperature, TOC

A few of the different models were tested for application to the Moorhead WTP. Those models that included data that was not collected in this research project were not tested. A more recent bromate prediction model by Lu et al. (2011), was selected for interpretation into Moorhead WTP data. The study measured bromate from two different water sources to determine the influence that changing water quality has on bromate formation. Changes in water sources provided for changes in both TOC and bromide as was consistent with Moorhead WTP influent water. Also, the research idea fit well within the scope of the research project conducted for Moorhead as many of the parameters considered were included in the study conducted at Moorhead. In the first stage of the modeling efforts by Lu et al. (2011), the parameters of TOC, UV254, ozone dose, time, bromide, pH, and temperature were considered. The results of the initial model provided a low β parameter for the time variable. The authors suggested that because the treatment facility that was studied contained four contactors, the flow in each was generally relatively stable, and the variable was removed from the model. The study also refined the model once more data was available in later years. The final model developed through this research effort is found as equation 10. It was found that all variables had a positive effect on bromate formation except for TOC which had a negative effect (Lu et al., 2011).

$$BrO_3 = e^{\beta_0} \times TOC_{inf}{}^{\beta_1} \times UV_{inf}{}^{\beta_2} \times D_{ozone}{}^{\beta_3} \times Br^{\beta_4} \times pH^{\beta_5} \times Temp^{\beta_6} \tag{10}$$

6.2. Past Bromate Prediction Model Application to Moorhead WTP Data

To improve the model to better fit those constraints set at the Moorhead WTP, a least-squares regression was applied to determine the β coefficients that minimized the difference in the residual values between the predicted and measured bromate values. After refining the model, the correlation coefficient was 0.78. The formation of bromate at the Moorhead WTP was found to follow a regression model in the form of Equation 11.

$$BrO_3 = e^{-9.180} \times TOC^{-0.479} \times UV254^{0.059} \times Ozone_{dose}{}^{1.281} \times Bromide^{0.899} \times pH^{4.461} \times Temp^{0.828} \tag{11}$$

6.3. Moorhead WTP Final Bromate Prediction Model

The UV254 variable in the model had the smallest β parameter of the variables considered. One requirement set by the Moorhead WTP was to make the model as simple as possible without losing a great degree of accuracy so implementation into their SCADA system at the WTP would be straightforward. To meet this requirement, the Moorhead bromate prediction model was simplified by removing the UV254 parameter. The removal of the parameter did not have a substantial effect on the results of the model, validating the decision of its removal. The final bromate prediction model follows Equation 12 for the Moorhead WTP.

$$BrO_3 = e^{-9.252} \times TOC^{-0.446} \times {Ozone_{dose}}^{1.279} \times Bromide^{0.904} \times pH^{4.398} \times Temp^{0.819} \quad (12)$$

The prediction model produced a correlation coefficient of 0.78 but contained variability as shown in Figure 52 through the points that lie outside of the ±20% lines. The modeled data provides a good trend in data but a high amount of variability in the data is observed as described by the median relative percentage difference of 28.5%.

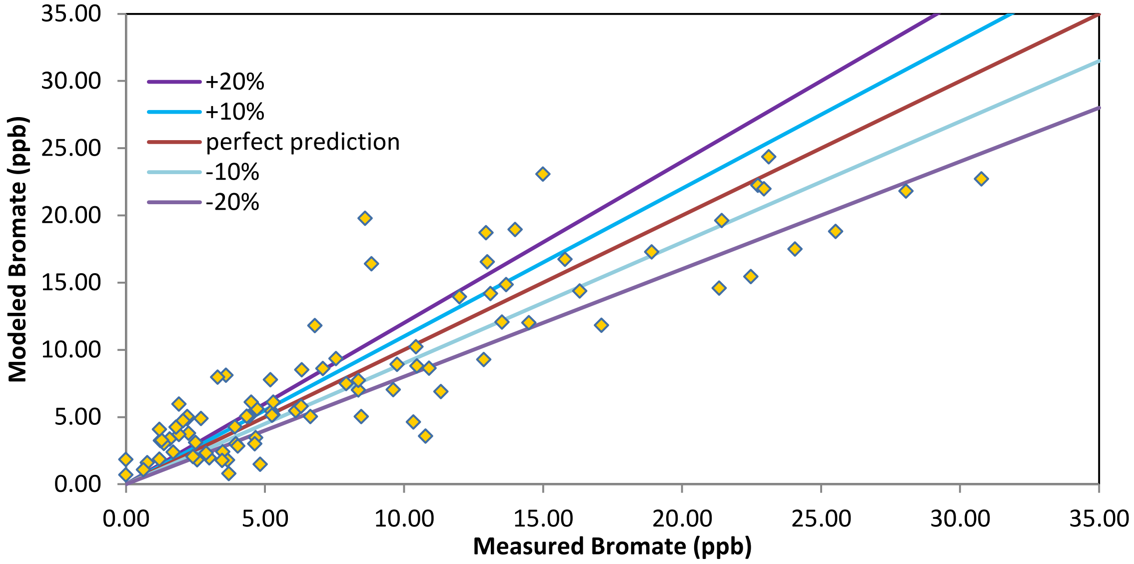

Figure 52: Moorhead WTP final bromate prediction model correlation

To determine how well the model captures the day to day changes in bromate formation, the modeled data was compared to the measured data over time (Figure 53). A new set of measured data was not utilized as bromate data was limited. It was observed that during the sampling period the model appears to be an under estimate during the summer months and an over estimate during the winter months, but is a good representation of the day to day changes in bromate formation at the Moorhead WTP.

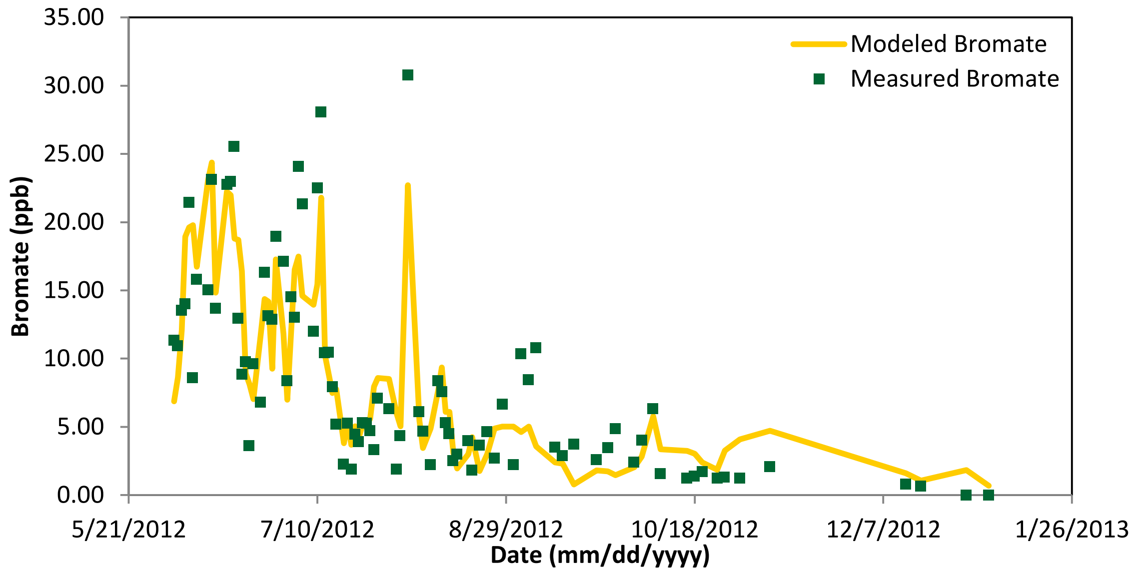

Figure 53: Modeled bromate vs. measured bromate over time at the Moorhead WTP

Through this prediction effort, it was determined that ozone dose, bromide concentration, pH, and temperature all have a positive correlation with bromate formation while TOC was found to have a negative correlation. Overall, the prediction model can be used to assist the Moorhead WTP in the optimization of their ozonation process to minimize bromate formation. The model utilizes easily monitored parameters that can be efficiently added to their already functioning SCADA system.

CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS

The conclusions drawn from the bromate research project conducted at the Moorhead WTP are based off of a conclusive study on past literature, a hands-on experience operating the Moorhead WTP, a full-scale sample and analysis approach, and mathematical modeling.

7.1. Overall Conclusions from Research

The overall goal of this project was to quantify the bromate formation in the disinfection process and identify operational strategies to minimize bromate formation. To meet this goal many objectives were carried out and conclusions were made. The major findings of this research are as follows:

- Bromide concentrations in the wells were quantified, determining that the Moorhead Aquifer wells contained the highest bromide concentrations on average near 0.30 ppm, followed by the Buffalo Aquifer wells with an average concentration of 0.07 ppm, and then the Red River with the lowest bromide concentration of the source waters with an average of 0.05 ppm.
- Bromate is forming at the Moorhead WTP in the ozone disinfection system, at times exceeding the MCL, and is a valid concern for the facility.
- Bromate formation occurs in all three sections of the ozone chamber and is highest in Sections 2 and 3 as compared to Section 1.
- The highest overall bromate concentrations formed during the summer months at Moorhead during the times of highest water temperature. Specifically, bromate formation exceeded the MCL of 10 ppb during times of water temperature greater than about 16°C.

- pH was observed to influence bromate formation in Sections 2 and 3 of the ozonation chamber at high temperatures but was found to be non-influential at all temperatures considered in Section 1.
- Section 1 of the ozonation chamber behaves differently due to the organic content found in this section. It was observed that Section 1 of the ozonation chamber reduced more organics for taste and odor removal than Sections 2 and 3.
- The organic content of the water in Section 1 of the ozonation chamber inhibits bromate formation in this section.
- Ozone dose was observed to be an influential parameter on bromate formation during those temperatures greater than approximately16°C with minimal influence at temperatures less than approximately 16°C.
- Variations in bromate formation were discovered day to day and were found to be attributed to changes in water plant operation controls.
- Water plant control changes can be used to develop strategies to aide in the minimization of bromate through source water choices and ozone dose applications.
- A bromate prediction model was developed to assist the Moorhead WTP in determining strategies to minimize bromate formation.
- Through the model development, the parameters of pH, ozone dose, temperature, and bromide had positive correlations with bromate formation while TOC was found to have a negative correlation with bromate.

7.2. Recommendations for Future Work

The conclusions drawn from this research effort are simply the beginning of what can be discovered concerning bromate formation on a full-scale system. Data validation would be the next step in an investigation into bromate formation in the Moorhead WTP ozonation system. Model validation should be considered to improve the prediction model for bromate formation and to reduce the relative percentage difference among the data points. The sample and analysis method developed for this project could be extended for another season and the data collected could be used to validate the model.

Further, bromate research at the Moorhead WTP could be extended to test some of the optimization strategies developed in the future by the Moorhead WTP staff. As the WTP begins to utilize the developed model for bromate prediction, it is expected that changes in operation will occur to assist in the minimization of bromate. The operational changes would be of great interest to the water treatment industry as many facilities move to include ozone in their disinfection process. One such strategy could be to maintain the winter pH depression method during the summer months. In the past, the Moorhead WTP utilized a lower pH in Section 1 of the ozonation chamber to minimize bromate formation during times of higher temperature and ozone dose. However, as was determined through this study, the organic content in the first section inhibits bromate formation and the influence of pH in Section 1 was found to be minimal on bromate formation. The WTP may want to maintain the high pH in Section 1 at all times of the year and study the effluent bromate formation as a result. If it was determined that bromate formation was not influenced by the higher pH in Section 1, better taste and odor removal would be possible at all times of the year and could improve the effluent water quality.

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APPENDIX

Table A1: Red River bromide, analysis by Fargo WTP

Bromide (ppm)							
Date	Red River	Date	Red River	Date	Red River	Date	Red River
8/9/10	0.037	3/21/11	0.046	10/31/11	0.074	6/11/12	0.038
8/16/10	0.034	3/28/11	0.043	11/7/11	0.073	6/18/12	0.031
8/22/10	0.035	4/4/11	0.035	11/14/11	0.073	6/25/12	0.047
8/30/10	0.029	4/11/11	0.021	11/21/11	0.09	7/2/12	0.039
9/7/10	<0.020	4/18/11	0.026	11/28/11	0.081	7/9/12	0.045
9/13/10	<0.020	4/25/11	0.035	12/5/11	0.073	7/16/12	0.039
9/20/10	0.026	5/2/11	0.051	12/12/11	0.059	7/23/12	0.044
9/27/10	0.034	5/9/11	0.044	12/19/11	0.059	7/30/12	0.042
10/4/10	0.046	5/16/11	0.043	12/27/11	0.053	8/6/12	0.039
10/11/10	0.052	5/23/11	0.047	1/2/12	0.038	8/13/12	0.043
10/18/10	0.024	5/31/11	0.091	1/9/12	<0.020	8/20/12	0.048
10/25/10	<0.020	6/6/11	0.051	1/16/12	0.050	8/29/12	0.059
11/1/10	0.047	6/13/11	0.050	1/23/12	0.040	9/4/12	0.065
11/8/10	0.049	6/20/11	0.059	1/30/12	0.042	9/10/12	0.060
11/15/10	0.046	6/27/11	0.047	2/6/12	0.039	9/17/12	0.046
11/22/10	0.062	7/4/11	0.056	2/13/12	0.035	9/24/12	0.047
11/29/10	0.070	7/11/11	0.053	2/21/12	0.047	10/1/12	0.043
12/6/10	0.045	7/18/11	0.032	2/27/12	0.048	10/8/12	0.050
12/13/10	0.082	7/25/11	0.063	3/5/12	0.039	10/15/12	0.057
12/20/10	0.044	8/1/11	0.061	3/12/12	0.045	10/23/12	0.048
12/28/10	0.045	8/8/11	0.056	3/19/12	0.041	10/29/12	0.04
1/3/11	0.041	8/15/11	0.069	3/26/12	0.076	11/5/12	0.067
1/10/11	0.035	8/22/11	0.068	4/2/12	0.067	11/14/12	0.057
1/17/11	0.033	8/29/11	0.082	4/9/12	0.059	11/19/12	0.052
1/24/11	0.031	9/5/11	0.080	4/16/12	0.054	11/26/12	0.073
1/31/11	0.046	9/12/11	0.081	4/23/12	0.062	12/3/12	0.053
2/7/11	0.037	9/19/11	0.082	4/30/12	0.168	12/10/12	0.063
2/15/11	0.036	9/26/11	0.073	5/7/12	0.061	12/17/12	0.061
2/23/11	0.058	10/3/11	0.086	5/14/12	0.066	12/24/12	0.051
2/28/11	0.041	10/11/11	0.066	5/21/12	0.056	12/31/12	0.047
3/7/11	0.045	10/17/11	0.055	5/28/12	0.043	1/7/13	0.040
3/14/11	0.054	10/24/11	0.085	6/4/12	0.037		

Table A2: Sample pH and temperature

Date	Time	Ozone Inf. #1		Ozone Inf. #2		Sect. 1		Sect. 2		Sect. 3	
		pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)
5/13/12	14:00										
5/15/12	17:00	11.17		11.18				9.52		9.54	
5/17/12	14:00	11.29		11.08							
5/20/12	19:00	11.35									
5/22/12	15:30	10.98		10.99							
5/23/12	13:00	11.04	17.4			10.60	18.1	9.66	17.8	9.60	17.7
5/24/12	17:00	11.03	17.6								
5/26/12	14:30	11.03	17.0								
5/27/12	16:00	10.90	16.0								
5/28/12	12:00	10.96	16.8								
5/29/12	15:00	11.00	17.4			9.48	17.8	9.48	17.8	9.44	17.8
5/30/12	10:00	11.00	17.2								
6/1/12	14:00	11.01				9.77				9.12	
6/2/12	14:00	11.09	17.6			9.21	18.1			9.34	18.3
6/3/12	14:00	11.05	17.6			8.98	17.6			9.34	17.9
6/4/12	13:00	11.09	17.7			9.65	18.2	9.50	18.4	9.44	18.0
6/5/12	16:00	11.07	18.3			9.64	18.8	9.57	18.6	9.53	18.5
6/6/12	14:00	11.11	18.8			9.73	19.6	9.59	19.3	9.56	19.2
6/7/12	8:00	10.77	19.4			9.70	19.9	9.49	19.7	9.42	19.6
6/8/12	8:00	10.91	19.7			9.33	20.2	9.20	20.1	9.08	20.0
6/11/12	8:30	10.89	20.3			9.32	21.5	9.35	22.0	9.28	21.9
6/12/12	7:00	11.08	19.9			9.42	21.3	9.37	21.7	9.34	21.7
6/13/12	6:00	10.86	18.9			9.36	20.3	9.35	20.3	9.32	20.4
6/16/12	16:30	10.90	20.2			9.40	20.7	9.33	20.7	9.28	20.5
6/17/12	15:00	10.87	20.3			9.43	20.7	9.34	20.6	9.28	20.6
6/18/12	15:30	10.95	19.6			9.63	20.0	9.46	19.9	9.40	19.8
6/19/12	15:45	11.09	19.0			9.60	19.6	9.54	19.4	9.52	19.4
6/20/12	22:00	11.08	20.8			9.16	20.7	9.14	20.8	9.14	20.8
6/21/12	15:30	11.08	18.3			9.51	18.9	9.26	18.8	9.23	18.8
6/22/12	17:45	10.95	18.5			9.33	19.2	9.31	19.0	9.21	18.8
6/23/12	17:00	11.07	18.6			9.41	19.1	9.17	18.8	9.18	18.8
6/25/12	15:00	10.93	19.4			9.38	20.0	9.08	20.0	9.06	19.8
6/26/12	15:00	10.96	18.9	10.73	18.4	9.33	18.9	9.18	18.7	9.15	18.7
6/27/12	9:30	10.85	19.0			9.30	19.6	9.23	19.4	9.24	19.6
6/28/12	14:45	11.00	17.8			9.48	18.4	9.32	18.2	9.33	18.1
6/29/12	16:30	11.00	19.4			9.53	19.7	9.26	19.6	9.25	19.5

Table A2: Sample pH and temperature (continued)

Date	Time	Ozone Inf. #1		Ozone Inf. #2		Sect. 1		Sect. 2		Sect. 3	
		pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)
6/30/12	17:00	11.03	19.3			9.31	19.8	9.24	19.5	9.15	19.5
7/1/12	18:00	11.00	19.0			9.17	19.4	9.15	19.1	9.06	19.2
7/2/12	16:30	10.95	19.2	11.11	19	9.33	19.0	9.06	18.8	9.00	18.8
7/3/12	15:30	10.70	19.8	10.97	19.5	9.11	19.8	8.98	19.9	8.98	19.6
7/4/12	11:00	10.85	20.8			9.14	20.7	9.08	20.7	8.95	20.6
7/5/12	8:30	11.02	20.4			9.25	20.7	9.28	21.5	9.26	21.3
7/6/12	9:00	10.99	20.2			9.19	21.5	9.18	21.2	9.13	21.4
7/9/12	15:00	10.93	17.6	10.81	17.6	9.52	17.7	9.47	17.6	9.54	17.4
7/10/12	16:30	11.14	17.3	11.05	17.3	9.48	17.7	9.46	17.4	9.48	17.1
7/11/12	16:30	11.11	17.9	11.06	17.8	9.64	18.0	9.67	17.8	9.66	17.8
7/12/12	14:00	11.08	17.7	11.13	17.5	9.64	18.0	9.37	17.6	9.35	17.6
7/13/12	10:00	11.11	17.5	11.13	17.5	9.56	17.9	9.43	17.6	9.40	17.5
7/14/12	18:00	10.95	17.7	11.06	17.4	9.47	18.3	9.41	17.8	9.39	17.8
7/15/12	18:00	10.83	17.4	11.06	17.1	9.40	17.8	9.37	17.3	9.36	17.1
7/17/12	8:00	11.06	15.3	10.94	15	9.39	15.6	9.23	15.4	9.23	15.3
7/18/12	14:30	11.21	17.3	11.21	17	9.46	17.4	9.21	17.1	9.20	16.9
7/19/12	16:30	10.95	15.8	10.99	15.5	9.24	15.8	9.13	15.6	9.12	15.3
7/20/12	9:00	10.87	20.1	10.96	20.3	9.18	19.5	9.25	19.4	9.22	19.4
7/21/12	18:00	10.89	16.9	11.02	16.9	9.41	17.8	9.33	17.1	9.27	16.9
7/22/12	14:00	11.09	17.3	11.03	17.1	9.42	17.6	9.32	17.2	9.28	17.1
7/23/12	13:30	11.05	17.6	11.10	17.3	9.35	17.9	9.21	17.6	9.25	17.4
7/24/12	10:30	11.05	16.3	10.96	16	9.56	16.4	9.33	16.4	9.31	16.1
7/25/12	14:30			11.14	17.4	9.41	17.7	9.26	17.3	9.22	17.0
7/26/12	12:00	10.93	17.9			9.27	18.2	9.27	18.0	9.25	17.9
7/29/12	14:00	10.86	17.3	10.85	17.1	9.40	17.6	9.25	17.3	9.21	17.0
7/31/12	11:00	10.92	16.9	10.96	16.6	9.27	17.1	9.31	16.8	9.27	16.7
8/1/12	15:30	10.91	17.5	10.96	17.2	9.24	17.5	9.26	17.2	9.23	17.3
8/3/12	18:00	11.30	19.8			9.38	19.9	9.33	19.9	9.27	19.8
8/6/12	14:00	10.97	16.7	10.99	16.5	9.51	16.9	9.35	16.7	9.34	16.6
8/7/12	14:00	10.92	16.2	11.01	15.9	9.35	16.3	9.23	16.2	9.18	16.3
8/9/12	16:00	11.02	17.8			9.32	18.1	9.18	18.1	9.07	18.3
8/11/12	18:00	10.97	19.7			8.81	19.8	8.81	19.9	8.81	20.1
8/12/12	18:00	10.84	19.4			9.00	19.6	9.00	19.5	8.93	19.8
8/13/12	14:00	10.99	17.5			9.13	18.0	9.12	17.9	9.16	18.0
8/14/12	21:00	11.08	20.1	10.95	20.2	9.12	16.9	9.13	17.1	9.15	17.1
8/15/12	18:00	11.12	15.9	11.04	15.6	9.10	16.1	9.16	15.8	9.15	15.6

Table A2: Sample pH and temperature (continued)

Date	Time	Ozone Inf. #1		Ozone Inf. #2		Sect. 1		Sect. 2		Sect. 3	
		pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)
8/16/12	16:00	11.02	15.5	11.04	15.2	9.26	15.7	9.23	15.6	9.16	15.6
8/19/12	19:00	10.93	15.4			9.34	15.7	9.29	15.3	9.31	15.3
8/20/12	12:00	11.18	15.2			9.35	15.5	9.27	15.4	9.22	15.1
8/22/12	10:00	10.95	16.7			9.18	17.1	9.19	17.3	9.20	17.4
8/24/12	12:00	11.03	15.7	11.08	15.3	9.34	15.7	9.34	15.6	9.26	15.4
8/26/12	17:30	11.03	16.2	11.05	15.9	9.30	16.1	9.25	15.9	9.28	15.8
8/28/12	14:00	11.04	15.6	10.93	15.1	9.57	15.5	9.52	15.3	9.51	15.4
8/31/12	15:00	10.96	15.9	11.03	15.6	9.42	16.1	9.44	15.7	9.40	15.7
9/2/12	22:00	10.97	17.3			9.31	15.7	9.34	16.0	9.35	16.0
9/4/12	16:00	10.94	15.5	10.89	15.1	9.49	15.6	9.47	15.6	9.43	15.3
9/6/12	15:30	11.22	16.4			9.46	16.4	9.45	16.3	9.44	16.3
9/11/12	15:30	11.01	14.5	11.01	14.3	9.47	14.4	9.45	14.3	9.43	14.2
9/13/12	17:30	11.05	14.2			9.53	14.5	9.45	14.5	9.41	14.2
9/16/12	21:30	11.33	14.6			9.44	14.5	9.29	14.6	9.26	14.5
9/22/12	18:00	11.10	13.0			9.53	12.7	9.35	12.7	9.33	12.7
9/25/12	15:30	11.08	12.2			10.74	12.8	9.62	12.7	9.59	12.3
9/27/12	16:30	11.34	11.7	11.34	11.3	10.37	11.7	9.59	12.0	9.59	11.6
10/2/12	15:30	11.35	12.1	11.28	11.8	11.10	12.3	9.79	12.3	9.57	12.3
10/4/12	8:00			11.09	12.8	10.48	13.0	9.69	13.1	9.68	13.2
10/7/12	12:00			11.28	11.3	11.01	11.8	9.67	11.5	9.68	11.9
10/9/12	15:00			11.35	11.4	11.00	11.5	9.61	11.4	9.65	11.5
10/16/12	8:30			11.19	11.5	10.90	10.9	9.79	11.1	9.84	11.6
10/18/12	13:00			11.39	10.2	11.24	10.7	9.89	10.6	9.94	11.5
10/20/12	13:00			11.26	10.1	11.14	9.8	9.85	9.8	9.86	10.8
10/24/12	10:00			11.24	10.1	11.14	10.1	9.77	10.4	9.77	11.3
10/26/12	15:00			11.44	9.7	10.75	10.2	9.68	10.2	9.71	11.1
10/30/12	16:00			11.41	9.7	11.13	10.1	9.75	10.2	9.74	10.9
11/7/12	14:30			11.50	8.7	11.19	8.9	9.69	8.7	9.70	8.9
12/13/12	15:30			11.53	5.3	11.09	5.50	9.64	5.4	9.6	6
12/17/12	15:00			11.71	4.7	11.36	5.40	9.61	5	9.59	5.8
12/29/12	13:30			11.77	4.4	11.34	5	9.73	4.6	9.65	5.3
1/4/13	17:00			11.63	4.9	10.87	5.6	9.61	5.2	9.67	6

Table A3: Ozone influent TOC with ozone dose

Date	Time	Ozone Inf. TOC	Ozone Dose	Date	Time	Ozone Inf. TOC	Ozone Dose
		mg/L	mg/L			mg/L	mg/L
5/13/12	14:00	2.97	3.6	7/19/12	16:30	2.55	2.0
5/15/12	17:00	5.12	5.6	7/20/12	9:00	2.61	2.3
5/17/12	14:00	3.25	5.6	7/21/12	18:00	2.02	2.0
5/20/12	19:00	3.12	6.2	7/22/12	14:00	2.03	2.4
5/22/12	15:30	3.11	7.1	7/23/12	13:30	2.53	2.5
5/23/12	13:00	3.04	6.9	7/24/12	10:30	2.08	2.2
5/24/12	17:00	3.45	6.9	7/25/12	14:30	2.09	3.0
5/26/12	14:30	3.54	6.2	7/26/12	12:00	2.23	3.2
5/27/12	16:00	3.44	5.8	7/29/12	14:00	2.19	3.4
5/28/12	12:00	3.24	6.5	7/31/12	11:00	2.21	2.6
5/29/12	15:00	3.36	6.9	8/1/12	15:30	2.15	2.7
5/30/12	10:00	3.75	6.6	8/3/12	18:00	2.97	6.0
6/1/12	14:00	3.75	6.7	8/6/12	14:00	2.19	2.7
6/2/12	14:00	4.20	5.6	8/7/12	14:00	2.16	2.5
6/3/12	14:00	3.99	5.4	8/9/12	16:00	2.84	3.1
6/4/12	13:00	4.49	6.5	8/11/12	18:00	3.31	4.9
6/5/12	16:00	3.41	6.9	8/12/12	18:00	3.63	5.3
6/6/12	14:00		6.9	8/13/12	14:00	2.95	3.6
6/7/12	8:00	3.20	6.9	8/14/12	21:00	2.92	3.9
6/8/12	8:00	3.67	6.9	8/15/12	18:00	2.40	3.2
6/11/12	8:30	3.33	6.9	8/16/12	16:00	2.03	2.2
6/12/12	7:00	3.28	6.9	8/19/12	19:00	3.31	2.3
6/13/12	6:00	3.09	5.8	8/20/12	12:00	2.06	2.2
6/16/12	16:30	3.17	6.9	8/22/12	10:00	2.12	2.2
6/17/12	15:00	3.22	6.9	8/24/12	12:00	2.05	2.4
6/18/12	15:30	3.07	6.9	8/26/12	17:30	2.17	2.6
6/19/12	15:45	2.78	6.7	8/28/12	14:00	2.44	2.4
6/20/12	22:00	2.97	5.0	8/31/12	15:00	2.15	2.3
6/21/12	15:30	2.95	4.0	9/2/12	22:00	2.28	3.1
6/22/12	17:45	2.67	3.8	9/4/12	16:00	2.53	3.0
6/23/12	17:00	3.10	3.6	9/6/12	15:30	2.88	3.2
6/25/12	15:00	2.94	4.7	9/11/12	15:30	2.31	2.1
6/26/12	15:00	3.19	5.0	9/13/12	17:30	2.26	2.2
6/27/12	9:30	2.75	4.9	9/16/12	21:30	2.22	2.0
6/28/12	14:45	2.57	4.0	9/22/12	18:00	2.41	2.0
6/29/12	16:30	2.76	5.3	9/25/12	15:30	2.39	2.3
6/30/12	17:00	2.84	5.0	9/27/12	16:30	1.94	2.0

Table A3: Ozone influent TOC with ozone dose (continued)

Date	Time	Ozone Inf. TOC	Ozone Dose	Date	Time	Ozone Inf. TOC	Ozone Dose
		mg/L	mg/L			mg/L	mg/L
7/1/12	18:00	2.80	4.4	10/2/12	15:30	1.92	2.2
7/2/12	16:30	2.87	3.2	10/4/12	8:00	3.39	3.3
7/3/12	15:30	2.83	4.5	10/7/12	12:00	4.51	6.0
7/4/12	11:00	2.84	5.7	10/9/12	15:00	4.13	4.5
7/5/12	8:30	2.46	5.5	10/16/12	8:30	1.25	2.0
7/6/12	9:00	4.06	6.1	10/18/12	13:00	0.95	1.8
7/9/12	15:00	2.14	4.8	10/20/12	13:00	0.99	1.5
7/10/12	16:30	2.90	5.0	10/24/12	10:00	0.94	1.6
7/11/12	16:30	2.98	6.0	10/26/12	15:00	NA	3.2
7/12/12	14:00	2.87	3.8	10/30/12	16:00	2.40	3.2
7/13/12	10:00	2.68	3.3	11/7/12	14:30	3.08	3.6
7/14/12	18:00	2.35	2.9	12/13/12	15:30	3.19	2.9
7/15/12	18:00	2.20	2.9	12/17/12	15:00	3.09	2.6
7/17/12	8:00	1.97	1.8	12/29/12	13:30	3.43	2.6
7/18/12	14:30	2.43	2.3	1/4/13	17:00	3.17	2.0

Table A4: UV254 values

Date	Time	UV254				
		Ozone Inf. #1	Ozone Inf. #2	Sect. #1	Sect. #2	Sect. #3
8/15/12	18:00	0.024	0.023	0.013	0.011	0.010
8/16/12	16:00					
8/19/12	19:00					
8/20/12	12:00	0.025		0.010	0.009	0.008
8/22/12	10:00					
8/24/12	12:00					
8/26/12	17:30	0.022	0.022	0.015	0.012	0.009
8/28/12	14:00					
8/31/12	15:00	0.021	0.021	0.012	0.011	0.008
9/2/12	22:00					
9/4/12	16:00	0.022	0.024	0.013	0.011	0.010
9/6/12	15:30	0.026		0.016	0.013	0.010
9/11/12	15:30	0.020	0.020	0.012	0.011	0.008
9/13/12	17:30	0.020		0.011	0.010	0.010
9/16/12	21:30	0.024		0.014	0.013	0.013
9/22/12	18:00	0.025		0.016	0.014	0.014
9/25/12	15:30	0.026		0.019	0.015	0.014
9/27/12	16:30	0.018	0.018	0.009	0.006	0.006
10/2/12	15:30	0.019	0.019	0.013	0.016	0.013
10/4/12	8:00		0.034	0.019	0.016	0.015
10/7/12	12:00		0.057	0.037	0.025	0.024
10/9/12	15:00		0.051	0.031	0.022	0.020
10/16/12	8:30		0.013	0.009	0.007	0.007
10/18/12	13:00		0.000	0.001	0.002	0.003
10/20/12	13:00		NA	NA	NA	NA
10/24/12	10:00		0.011	0.009	0.009	0.001
10/26/12	15:00		0.035	0.023	0.018	0.013
10/30/12	16:00		0.027	0.017	0.013	0.013
11/7/12	14:30		0.033	0.023	0.016	0.015
12/13/12	15:30		0.033	0.022	0.019	0.016
12/17/12	15:00		0.030	0.022	0.018	0.017
12/29/12	13:30		0.035	0.024	0.022	0.021
1/4/13	17:00		0.029	0.020	0.018	0.018

Table A5: Bromate concentrations, analysis by Eaton Analytical

Date		Bromate (ppb)	
Sample	Analysis	Sect. 1	Sect. 3
6/5/2012	8/15/2012	3.60	14.00
6/7/2012	9/17/2012	1.10	8.60
6/11/2012	8/15/2012	3.40	15.00
6/19/2012	9/17/2012	1.20	7.00
6/22/2012	9/18/2012	0.00	3.60
6/25/2012	8/15/2012	1.40	6.80
6/28/2012	8/15/2012	0.00	6.20
7/4/2012	8/15/2012	3.40	13.00
7/9/2012	8/15/2012	2.80	12.00
7/11/2012	9/18/2012	3.80	16.00
7/15/2012	8/15/2012	1.10	5.20
7/19/2012	8/15/2012	0.00	1.90
7/25/2012	9/18/2012	0.00	3.30
7/31/2012	9/18/2012	0.00	1.90
8/3/2012	9/18/2012	7.90	19.00
8/9/2012	9/18/2012	0.00	2.20
8/15/2012	9/18/2012	0.00	2.50
8/20/2012	9/18/2012	0.00	1.80
8/26/2012	9/18/2012	0.00	2.70
8/31/2012	9/18/2012	0.00	2.20

Table A6: Bromide analysis #1 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovered/Difference	
				%	Requirement
1	Blank	n.a.	0	0.00	≤ MDL
2	CCC (Std 1)	0.08	0.15	53.33	75 % to 125 %
3	LFSSM CCC (Std 5+Fort)	5.852	6	85.20	75 % to 125 %
4	LFB (QC1ppm))	0.855	1	85.50	75 % to 125 %
7	SE FORT 06/19/2012	0.916	1.024	89.20	75 % to 125 %
8	SE Dup 06/19/2012	0.024	0.024	0.00	± 20%
17	CCC (Std 4)	2.248	2.5	89.92	75 % to 125 %
28	CCC (Std 6)	9.39	10	93.90	75 % to 125 %
32	FI FORT 07/09/2012	0.93	1.038	89.20	75 % to 125 %
33	FI FORT DUP 07/09/2012	0.924	1.038	0.65	± 20%
40	Std 2	0.39	0.5	78.00	75 % to 125 %
41	Std 4	2.208	2.5	88.32	75 % to 125 %
42	Blank	n.a.	0	0.00	≤ MDL

Table A7: Bromide analysis #1 ozone influent sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
6	SE 06/19/2012	9/19/2012	0.024	2,4
11	SE #1 06/22/2012	9/19/2012	0.024	2,4
16	SE 06/25/2012	9/19/2012	0.037	2,4
20	SE 06/28/2012	9/19/2012	0.026	2,4
23	SE #1 07/04/2012	9/19/2012	0.053	2,4
24	SE #2 07/04/2012	9/19/2012	0.053	2,4
29	SE #1 07/09/2012	9/20/2012	0.06	2,4
30	SE #2 07/09/2012	9/20/2012	0.039	2,4
34	SE #1 07/11/2012	9/20/2012	0.061	2,4
35	SE #2 07/11/2012	9/20/2012	0.062	2,4

Table A8: Bromide analysis #1 groundwater sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
9	Well 2 @ well 06/19/2012	9/19/2012	0.027	2,4
14	well 8 @ well 06/25/2012	9/19/2012	0.044	2,4
39	Well 9 @well 07/16/2012	9/20/2012	0.050	2,4
37	Well 1 @well 07/16/2012	9/20/2012	0.026	2,4
38	Well 10 @well 07/17/2012	9/20/2012	0.048	2,4

[1] Samples were analyzed outside of the proper recovery for CCC standards
[2] Sample concentrations were less than the MRL
[3] Sample concentrations were greater than the highest calibration standard
[4] Samples were analyzed after the 28 day holding period
[5] Samples were analyzed outside of the proper difference for duplicate samples
[6] Samples were analyzed outside of the proper recovery for fortified samples

Table A9: Bromide analysis #2 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovered/Difference	
				%	Requirement
1	Blank	n.a.	0	0.00	≤ MDL
2	Std 2	0.497	0.5	99.40	75 % to 125 %
3	Std 1	0.111	0.15	74.00	75 % to 125 %
6	10/30/2012 FI Fort	1.051	1	105.10	75 % to 125 %
7	10/30/2012 FI Dup	0.065	0	-200.00	± 20%
19	FORT BLANK	1.046	1	104.60	75 % to 125 %
23	10/7/2012 SE FORT	1.104	1.055	104.90	75 % to 125 %
24	10/7/2012 SE DUP	0.065	0.055	-16.67	± 20%
29	CCC (STD 5)	5.093	5	101.86	75 % to 125 %
33	10/2/2012 SE 2 FORT	1.061	1.049	101.20	75 % to 125 %
34	10/2/2012 SE 2 DUP	0.044	0.049	10.75	± 20%
43	FORT BLANK	1.033	1	103.30	75 % to 125 %
52	BLANK	n.a.	0	0.00	≤ MDL
53	CCC (STD 2)	0.516	0.5	103.20	75 % to 125 %
57	9/27/2012 FI FORT	1.086	1.039	104.70	75 % to 125 %
58	9/27/2012 FI DUP	0.049	0.039	-22.73	± 20%
66	FORT BLANK	1.059	1	105.90	75 % to 125 %
77	BLANK	n.a.	0	0.00	≤ MDL
78	CCC (STD 4)	2.84	2.5	113.60	75 % to 125 %
82	8/22/2012 RIVER FORT	1.164	1.051	111.30	75 % to 125 %
83	8/22/2012 RIVER DUP	0.052	0.051	-1.94	± 20%
91	FORT BLANK	1.087	1	108.70	75 % to 125 %
102	BLANK	n.a.	0	0.00	≤ MDL
103	CCC (STD 6)	8.942	10	89.42	75 % to 125 %
106	9/11/2012 F FORT	1.208	1.051	115.70	75 % to 125 %
107	9/11/2012 F DUP	0.052	0.051	-1.94	± 20%
116	FORT BLANK	1.123	1	112.30	75 % to 125 %
127	BLANK	n.a.	0	0.00	≤ MDL
128	CCC (STD 2)	0.166	0.5	33.20	75 % to 125 %

Table A10: Bromide analysis #2 ozone influent sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
4	10/30/2012 SE	10/30/2012	0.074	2
8	10/26/2012 SE	10/30/2012	0.038	2,5
11	10/24/2012 SE	10/30/2012	0.05	2,5
13	10/20/2012 SE	10/30/2012	0.073	2,5
15	10/18/2012 SE	10/31/2012	0.066	2,5
17	10/16/2012 SE	10/31/2012	0.077	2,5
20	10/9/2012 SE	10/31/2012	0.046	2,5
22	10/7/2012 SE	10/31/2012	0.055	2
26	10/4/2012 SE	10/31/2012	0.044	2
31	10/2/2012 SE 1	10/31/2012	0.059	2
32	10/2/2012 SE 2	10/31/2012	0.049	2
36	6/4/2012 SE	10/31/2012	0.082	2,4
38	6/3/2012 SE	10/31/2012	0.086	2,4
40	6/2/2012 SE	10/31/2012	0.059	2,4
42	6/1/2012 SE	10/31/2012	0.069	2,4
45	5/30/2012 SE	10/31/2012	0.047	2,4
47	5/28/2012 SE	10/31/2012	0.103	2,4
49	5/27/2012 SE	10/31/2012	0.092	2,4
54	9/27/2012 SE#1	11/1/2012	0.064	2,4
55	9/27/2012 SE#2	11/1/2012	0.034	2,4
59	9/22/2012 SE	11/1/2012	0.058	2,4,5
61	9/16/2012 SE	11/1/2012	n.a.	2,4,5
63	9/13/2012 SE	11/1/2012	0.055	2,4,5
65	9/11/2012 SE #1	11/1/2012	0.072	2,4,5
67	9/11/2012 SE #2	11/1/2012	0.053	2,4
68	9/6/2012 SE	11/1/2012	0.052	2,4
69	9/4/2012 SE #1	11/1/2012	0.077	2,4
70	9/4/2012 SE #2	11/1/2012	0.087	2,4
72	9/2/2012 SE	11/1/2012	0.07	2,4
74	9/25/2012 SE #1	11/1/2012	0.041	2,4
79	8/24/2012 SE #1	11/1/2012	0.072	2,4
80	8/24/2012 SE #2	11/1/2012	0.055	2,4
84	8/22/2012 SE	11/1/2012	0.039	2,4
86	8/14/2012 SE #1	11/1/2012	0.082	2,4
87	8/14/2012 SE #2	11/1/2012	0.077	2,4
115	8/7/2012 SE #1	11/2/2012	0.074	2,4
117	8/7/2012 SE #2	11/2/2012	0.066	1,2,4
119	8/16/2012 SE #1	11/2/2012	0.05	1,2,4
120	8/16/2012 SE #2	11/2/2012	0.042	1,2,4

Table A10: Bromide analysis #2 ozone influent sample concentrations (continued)

#	Sample	Analysis Date	Bromide (ppm)	Notes
122	8/19/2012 SE	11/2/2012	0.078	1,2,4
124	8/1/2012 SE #1	11/2/2012	0.086	1,2,4
125	8/1/2012 SE #2	11/2/2012	0.101	1,2,4

[1] Samples were analyzed outside of the proper recovery for CCC standards
[2] Sample concentrations were less than the MRL
[4] Samples were analyzed after the 28 day holding period
[5] Samples were analyzed outside of the proper difference for duplicate samples

Table A11: Bromide analysis #2 ozone effluent sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
89	10/2/2012 F	11/1/2012	0.048	2,4
90	10/4/2012 F	11/1/2012	0.051	2
92	10/7/2012 F	11/1/2012	0.061	2
93	10/9/2012 F	11/2/2012	0.051	2
94	10/16/2012 F	11/2/2012	0.11	2
95	10/18/2012 F	11/2/2012	0.055	2
96	10/20/2012 F	11/2/2012	0.087	2
97	10/24/2012 F	11/2/2012	0.056	2
98	10/26/2012 F	11/2/2012	0.049	2
99	10/30/2012 F	11/2/2012	0.06	2
100	9/2/2012 F	11/2/2012	0.076	2,4
101	9/4/2012 F	11/2/2012	0.09	2,4
104	9/6/2012 F	11/2/2012	0.069	2,4
105	9/11/2012 F	11/2/2012	0.051	2,4
108	9/13/2012 F	11/2/2012	0.052	2,4
109	9/16/2012 F	11/2/2012	0.045	2,4
110	9/22/2012 F	11/2/2012	0.061	2,4
111	9/25/2012 F	11/2/2012	0.056	2,4
112	9/27/2012 F	11/2/2012	0.051	2,4
113	8/14/2012 F	11/2/2012	0.088	2,4
114	8/24/2012 F	11/2/2012	0.057	2,4
118	8/7/2012 F	11/2/2012	0.069	1,2,4
121	8/16/2012 F	11/2/2012	n.a.	1,2,4
123	8/19/2012 F	11/2/2012	0.071	1,2,4

[1] Samples were analyzed outside of the proper recovery for CCC standards
[2] Sample concentrations were less than the MRL
[4] Samples were analyzed after the 28 day holding period

Table A12: Bromide analysis #2 groundwater sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
30	10/4/2012 @WELL 9	10/31/2012	0.053	[2]

[2] Sample concentrations were less than the MRL

Table A13: Bromide analysis #3 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovery/Difference	
				%	Requirement
1	Blank	0	0	0.00	≤ MDL
2	Blank	0	0	0.00	≤ MDL
3	Blank	0	0	0.00	≤ MDL
4	Std 5	4.9971	5	99.94	75 % to 125 %
5	Std 4	2.5012	2.5	100.05	75 % to 125 %
6	Std 3	1.0285	1	102.85	75 % to 125 %
7	Std 2	0.4698	0.5	93.96	75 % to 125 %
8	Std 1	0.1032	0.15	68.80	75 % to 125 %
9	Blank	0	0	0.00	≤ MDL
10	Std 1	0.145	0.15	96.67	75 % to 125 %
11	Std 2	0.4504	0.5	90.08	75 % to 125 %
14	8/3/2012 SE #1 FORT	1.0204	1.1467	87.37	75 % to 125 %
15	8/3/2012 SE #1 DUP	0.1037	0.1467	34.35	± 20%
16	BLANK	0	0	0.00	≤ MDL
24	FORT BLANK	0.9215	1	92.15	75 % to 125 %
34	BLANK	0	0	0.00	≤ MDL
35	CCC (STD 3)	0.9241	1	92.41	75 % to 125 %
43	8/28/2012 F FORT	1.4016	1.1044	129.72	75 % to 125 %
44	8/28/2012 F DUP	0.1058	0.1044	-1.33	± 20%
49	FORT BLANK	1.1619	1	116.19	75 % to 125 %
59	BLANK	0	0	0.00	≤ MDL
60	CCC (STD 4)	2.3794	2.5	95.18	75 % to 125 %
62	7/29/2012 F FORT	0.9823	1.1018	88.05	75 % to 125 %
63	7/29/2012 F DUP	0.1016	0.1018	0.20	± 20%
71	FORT BLANK	0.961	1	96.10	75 % to 125 %
82	BLANK	0	0	0.00	≤ MDL
83	CCC (STD 2)	0.4886	0.5	97.72	75 % to 125 %
86	Blank	0	0	0.00	≤ MDL
87	Std 1	0.1499	0.15	99.93	75 % to 125 %
88	Std 3	1.0589	1	105.89	75 % to 125 %
91	7/10/2012 NP FORT	1.2303	1.2129	101.74	75 % to 125 %
92	7/10/2012 NP DUP	0.2082	0.2129	2.23	± 20%
99	FORT BLANK	1.033	0	103.30	75 % to 125 %

Table A13: Bromide analysis #3 quality control (continued)

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovery/Difference	
				%	Requirement
109	CCC (STD 3)	0.9937	1	99.37	75 % to 125 %
113	7/5/2012 SE FORT	1.1088	1.1152	99.36	75 % to 125 %
114	7/5/2012 SE DUP	0.1124	0.1152	2.46	± 20%
122	FORT BLANK	1.0316	1	103.16	75 % to 125 %
133	BLANK	0	0	0.00	≤ MDL
134	CCC (STD 4)	2.6878	2.5	107.51	75 % to 125 %
141	7/29/2012 SE #1 FORT	1.1515	1.1168	103.47	75 % to 125 %
142	7/29/2012 SE #1 DUP	0.1152	0.1168	1.38	± 20%
147	FORT BLANK	1.0834	1	108.34	75 % to 125 %
158	BLANK	0	0	0.00	≤ MDL
159	CCC (STD 1)	0.1474	0.15	98.27	75 % to 125 %
160	CCC (STD 3)	1.0514	1	105.14	75 % to 125 %
163	6/18/2012 SE #1 FORT	1.0938	1.0946	99.92	75 % to 125 %
164	6/18/2012 SE #1 DUP	0.0951	0.0946	-0.53	± 20%
173	FORT BLANK	1.0506	1	105.06	75 % to 125 %
178	Blank	0	0	0.00	≤ MDL
179	Std 1	0.1483	0.15	98.87	75 % to 125 %
180	Std 3	1.0482	1	104.82	75 % to 125 %
181	Blank	0	0	0.00	≤ MDL
182	Blank	0	0	0.00	≤ MDL
183	Std 3	1.0579	1	105.79	75 % to 125 %
184	Std 1	0.1505	0.15	100.33	75 % to 125 %
185	Blank	0	0	0.00	≤ MDL

Table A14: Bromide analysis #3 ozone influent sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
13	8/3/2012 SE #1	11/16/2012	0.147	2,4
17	8/6/2012 SE #1	11/16/2012	0.089	2,4,5
18	8/6/2012 SE #2	11/16/2012	0.101	2,4,5
20	8/9/2012 SE	11/17/2012	0.082	2,4,5
25	8/11/2012 SE #1	11/17/2012	0.084	2,4
28	8/13/2012 SE	11/17/2012	0.092	2,4
30	8/15/2012 SE #1	11/17/2012	n.a.	2,4
31	8/15/2012 SE #2	11/17/2012	0.104	2,4
33	8/20/2012 SE	11/17/2012	0.110	2,4
37	8/26/2012 SE #1	11/17/2012	0.102	2,4,5
38	8/26/2012 SE #2	11/17/2012	0.093	2,4,5
40	8/28/2012 SE #1	11/17/2012	0.110	2,4,5
41	8/28/2012 SE #2	11/17/2012	0.105	2,4,5
47	8/31/2012 SE #1	11/17/2012	0.114	2,4
48	8/31/2012 SE #2	11/17/2012	0.111	2,4
51	11/7/2012 SE	11/17/2012	0.097	2
54	8/12/2012 SE	11/17/2012	0.090	2,4
66	7/22/2012 SE #2	11/18/2012	0.101	2,4
68	7/21/2012 SE	11/18/2012	0.102	2,4
70	7/14/2012 SE #1	11/18/2012	0.116	2,4
72	7/14/2012 SE #2	11/18/2012	0.115	2,4
76	7/13/2012 SE #1	11/18/2012	0.122	2,4
77	7/13/2012 SE #2	11/18/2012	0.124	2,4
79	7/12/2012 SE #1	11/18/2012	0.124	2.4
80	7/12/2012 SE #2	11/18/2012	0.122	2,4
93	7/10/2012 SE #1	11/19/2012	0.131	2,4
94	7/10/2012 SE #2	11/19/2012	0.133	2,4
96	7/6/2012 SE	11/19/2012	0.098	2,4
101	7/3/2012 SE #1	11/19/2012	0.127	2,4
102	7/3/2012 SE #2	11/19/2012	0.134	2,4
105	7/1/2012 SE	11/20/2012	0.127	2,4
106	7/2/2012 SE#1	11/20/2012	0.121	2,4
107	7/2/2012 SE#2	11/20/2012	0.123	2,4
110	7/4/2012 SE#1	11/20/2012	0.123	2,4
111	7/4/2012 SE#2	11/20/2012	0.126	2,4
112	7/5/2012 SE	11/20/2012	0.115	2,4
115	7/9/2012 SE #1	11/20/2012	0.107	2,4
116	7/9/2012 SE #2	11/20/2012	0.111	2,4
117	7/11/2012 SE #1	11/20/2012	0.134	2,4

Table A14: Bromide analysis #3 ozone influent sample concentrations (continued)

#	Sample	Analysis Date	Bromide (ppm)	Notes
118	7/11/2012 SE #2	11/20/2012	0.136	2,4
119	7/15/2012 SE #2	11/20/2012	0.123	2,4
120	7/17/2012 SE #1	11/20/2012	0.123	2,4
121	7/20/2012 SE #1	11/20/2012	0.109	2,4
123	7/20/2012 SE #2	11/20/2012	0.106	2,4
124	7/21/2012 SE #2	11/20/2012	0.110	2,4
125	7/22/2012 SE #1	11/20/2012	0.104	2,4
126	7/23/2012 SE #1	11/20/2012	0.102	2,4
127	7/23/2012 SE #2	11/20/2012	0.105	2,4
128	7/25/2012 SE #2	11/20/2012	0.123	2,4
129	7/31/2012 SE #2	11/20/2012	0.117	2,4
135	7/18/2012 SE #1	11/21/2012	0.126	2,4
136	7/18/2012 SE #2	11/21/2012	0.130	2,4
137	7/24/2012 SE #1	11/21/2012	0.135	2,4
138	7/24/2012 SE #2	11/21/2012	0.123	2,4
139	7/26/2012 SE	11/21/2012	0.124	2,4
140	7/29/2012 SE #1	11/21/2012	0.117	2,4
143	7/29/2012 SE #2	11/21/2012	0.115	2,4
144	7/15/2012 SE #1	11/21/2012	0.126	2,4
145	7/17/2012 SE #2	11/21/2012	0.121	2,4
146	7/19/2012 SE #1	11/21/2012	0.119	2,4
148	7/19/2012 SE #2	11/21/2012	0.119	2,4
149	7/31/2012 SE #1	11/21/2012	0.119	2,4
150	6/5/2012 SE #1	11/21/2012	0.102	2,4
151	6/6/2012 SE #1	11/21/2012	0.100	2,4
152	6/7/2012 SE #1	11/21/2012	0.101	2,4
153	6/8/2012 SE #1	11/21/2012	0.105	2,4
154	6/11/2012 SE #1	11/21/2012	0.126	2,4
155	6/12/2012 SE #1	11/21/2012	0.131	2,4
156	6/13/2012 SE #1	11/21/2012	0.101	2,4
157	6/16/2012 SE #1	11/21/2012	0.122	2,4
161	6/17/2012 SE #1	11/22/2012	0.120	2,4
162	6/18/2012 SE #1	11/22/2012	0.095	2,4
165	6/20/2012 SE #1	11/22/2012	0.145	2,4
166	6/21/2012 SE #1	11/22/2012	0.100	2,4
167	6/22/2012 SE #1	11/22/2012	0.095	2,4
168	6/23/2012 SE #1	11/22/2012	0.096	2,4
169	6/25/2012 SE #1	11/22/2012	0.111	2,4

Table A14: Bromide analysis #3 ozone influent sample concentrations (continued)

#	Sample	Analysis Date	Bromide (ppm)	Notes
170	6/26/2012 SE #1	11/22/2012	0.135	2,4
171	6/27/2012 SE #1	11/22/2012	0.131	2,4
172	6/28/2012 SE #1	11/22/2012	0.098	2,4
174	6/29/2012 SE #1	11/22/2012	0.126	2,4
175	6/30/2012 SE #1	11/22/2012	0.128	2,4
176	6/26/2012 SE #2	11/22/2012	0.137	2,4
177	6/19/2012 SE #1	11/22/2012	0.093	2,4

[2] Sample concentrations were less than the MRL
[4] Samples were analyzed after the 28 day holding period
[5] Samples were analyzed outside of the proper difference for duplicate samples

Table A15: Bromide analysis #3 ozone effluent bromide concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
19	8/6/2012 F	11/16/2012	0.0914	2,4,5
21	8/9/2012 F	11/17/2012	0.0887	2,4,5
26	8/11/2012 F	11/17/2012	0.1044	2,4
27	8/12/2012 F	11/17/2012	0.0833	2,4
29	8/13/2012 F	11/17/2012	0.0849	2,4
32	8/15/2012 F	11/17/2012	0.089	2,4
36	8/20/2012 F	11/17/2012	0.133	2,4,6
39	8/26/2012 F	11/17/2012	0.0918	2,4,6
42	8/28/2012 F	11/17/2012	0.1044	2,4,6
50	8/31/2012 F	11/17/2012	0.1158	2,4
52	11/7/2012 F	11/17/2012	0.0999	2
53	8/1/2012 F	11/17/2012	0.1057	2,4
55	8/22/2012 F	11/18/2012	0.096	2,4
61	7/29/2012 F	11/18/2012	0.1018	2,4
64	7/26/2012 F	11/18/2012	0.1081	2,4
65	7/23/2012 F	11/18/2012	0.095	2,4
67	7/22/2012 F	11/18/2012	0.097	2,4
69	7/20/2012 F	11/18/2012	0.0991	2,4
78	7/13/2012 F	11/18/2012	0.119	2,4
81	7/2/2012 F	11/18/2012	0.1137	2,4
84	7/11/2012 F	11/18/2012	0.1212	2,4

Table A15: Bromide analysis #3 ozone effluent bromide concentrations (continued)

#	Sample	Analysis Date	Bromide (ppm)	Notes
103	7/3/2012 F	11/20/2012	0.1281	2,4
108	7/31/2012 F	11/20/2012	0.1198	2,4

[2] Sample concentrations were less than the MRL
[4] Samples were analyzed after the 28 day holding period
[5] Samples were analyzed outside of the proper difference for duplicate samples
[6] Samples were analyzed outside of the proper recovery for fortified samples

Table A16: Bromide analysis #3 groundwater sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
12	8/3/2012 WELL MIX	11/16/2012	0.1562	4,5
23	8/11/2012 @WELL 1	11/17/2012	0.0801	2,4,5
46	8/31/2012 WELL MIX	11/17/2012	0.1217	4
56	11/2/2012 @WELL 2	11/18/2012	0.0886	2
57	11/2/2012 @WELL 1	11/18/2012	0.0875	2
58	7/3/2012 @ WELL 8	11/18/2012	0.1014	2,4
104	7/3/2012 @ Well 6	11/20/2012	0.299	4
130	7/17/2012 @WELL 10	11/20/2012	0.1201	2,4
131	7/16/2012 @ WELL 1	11/20/2012	0.0931	2,4
132	7/16/2012 @ WELL 9	11/20/2012	0.1299	2,4

[2] Sample concentrations were less than the MRL
[4] Samples were analyzed after the 28 day holding period
[5] Samples were analyzed outside of the proper difference for duplicate samples

Table A17: Bromide analysis #4 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovered/Difference %	Requirement
1	Blank	n.a.	0	0.00	≤ MDL
2	Std 1	0.105	0.15	70.00	75 % to 125 %
3	Std 2	0.474	0.5	94.80	75 % to 125 %
4	Std 3	0.9837	1	98.37	75 % to 125 %
5	Std 4	2.5572	2.5	102.29	75 % to 125 %
6	Std 5	4.9793	5	99.59	75 % to 125 %
7	LRB	n.a.	0	0.00	≤ MDL
8	IPC (Std 1)	0.1045	0.15	69.67	75 % to 125 %
9	LFB (1 ppb)	0.9702	1	97.02	75 % to 125 %
13	6/7/2012 RIVER FORT	1.0888	1.0545	103.43	75 % to 125 %
14	6/7/2012 RIVER DUP	0.0554	0.0545	-1.64	± 20%
20	CCC (Std 2)	0.4737	0.5	94.74	75 % to 125 %
22	6/17/2012 F Fort	1.107	1.0776	102.94	75 % to 125 %
23	6/17/2012 F Fort Dup	1.1085	1.0776	-2.83	± 20%
31	CCC (Std 3)	1.0018	1	-100.18	75 % to 125 %
32	LRB	n.a.	0	0.00	≤ MDL
33	LFB (1 ppb)	1.0441	1	104.41	75 % to 125 %
35	6/26/2012 F Fort	1.1609	1.0891	107.18	75 % to 125 %
37	6/26/2012 RIVER Dup	0.0722	0.0726	0.55	± 20%
44	CCC (Std 4)	2.6092	2.5	-104.37	75 % to 125 %
55	CCC (Std 2)	0.4926	0.5	-98.52	75 % to 125 %
56	LRB	n.a.	0	0.00	≤ MDL
57	LFB	1.0279	1	102.79	75 % to 125 %
59	7/24/2012 F Dup	0.0793	0.0814	2.61	± 20%
60	7/24/2012 F Fort	1.1339	1.0814	105.25	75 % to 125 %
62	std 5	5.0208	5	100.42	75 % to 125 %
65	CCC (Std 1)	0.1055	0.15	70.33	75 % to 125 %
66	Blank	n.a.	0	0.00	≤ MDL

Table A18: Bromide analysis #4 ozone effluent sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
10	6/6/2012 F	11/28/2012	0.0547	2,4
11	6/7/2012 F	11/28/2012	0.0614	2,4
15	6/8/2012 F	11/28/2012	0.0595	2,4
16	6/12/2012 F	11/28/2012	0.0823	2,4
17	6/13/2012 F	11/28/2012	0.0599	2,4
19	6/16/2012 F	11/28/2012	0.0763	2,4
21	6/17/2012 F	11/28/2012	0.0776	2,4
24	6/18/2012 F	11/29/2012	0.0503	2,4
25	6/19/2012 F	11/29/2012	0.049	2,4
26	6/20/2012 F	11/29/2012	0.0797	2,4
27	6/21/2012 F	11/29/2012	0.0528	2,4
29	6/22/2012 F	11/29/2012	0.0472	2,4
30	6/23/2012 F	11/29/2012	0.0487	2,4
34	6/26/2012 F	11/29/2012	0.0891	2,4
38	6/27/2012 F	11/29/2012	0.0888	2,4
39	6/28/2012 F	11/29/2012	0.0531	2,4
40	6/29/2012 F	11/29/2012	0.0803	2,4
41	6/30/2012 F	11/29/2012	0.0775	2,4
45	7/1/2012 F	11/29/2012	0.0888	2,4
46	7/5/2012 F	11/29/2012	0.0675	2,4
47	7/6/2012 F	11/29/2012	0.0699	2,4
48	7/10/2012 F	11/29/2012	0.0845	2,4
49	7/12/2012 F	11/29/2012	0.0912	2,4
50	7/14/2012 F	11/29/2012	0.0844	2,4
51	7/17/2012 F	11/30/2012	0.0803	2,4
53	7/18/2012 F	11/30/2012	0.0818	2,4
54	7/21/2012 F	11/30/2012	0.0749	2,4
58	7/24/2012 F	11/30/2012	0.0814	2,4

[2] Sample concentrations were less than the MRL

[4] Samples were analyzed after the 28 day holding period

Table A19: Bromide analysis #4 groundwater sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
63	11/30/2012 @ well 8	11/30/2012	0.0698	[2]
64	11/30/2012 @ well 9	11/30/2012	0.0863	[2]

[2] Sample concentrations were less than the MRL

Table A20: Bromide analysis #5 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovery/Difference	
				%	Requirement
1	Blank	n.a.	0.00	n.a.	≤ MDL
2	Std 1	0.0218	0.025	87.20	75 % to 125 %
3	Std 2	0.0484	0.050	96.80	75 % to 125 %
4	Std 3	0.0956	0.100	95.60	75 % to 125 %
5	Std 4	0.4761	0.500	95.22	75 % to 125 %
6	Std 5	1.0399	1.000	103.99	75 % to 125 %
7	Std 6	1.9875	2.000	99.38	75 % to 125 %
8	Blank	n.a.	0.000	n.a.	≤ MDL
9	CCC (Std1)	0.0234	0.025	93.60	75 % to 125 %
10	Blank	n.a.	0.000	n.a.	≤ MDL
11	CCC (Std1)	0.0246	0.025	98.40	75 % to 125 %
19	CCC (Std3)	0.095	0.100	95.00	75 % to 125 %
20	Blank	n.a.	0.000	n.a.	≤ MDL
23	F FORT 12/13/2012	0.5403	0.570	94.44	75 % to 125 %
24	F DUP 12/13/2012	0.062	0.068	-9.38	± 20%
33	CCC (STD 2)	0.0478	0.050	95.60	75 % to 125 %
37	LFB	0.5055	0.500	101.10	75 % to 125 %
38	CCC (STD 3)	0.0909	0.100	90.90	75 % to 125 %

Table A21: Bromide analysis #5 ozone influent sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
21	SE 12/13/2012	1/29/2013	0.0642	[4]
25	SE 12/17/2012	1/29/2013	0.0498	[4]
27	SE 12/29/2012	1/29/2013	0.0998	[4]
29	SE 1/4/2013	1/29/2013	0.0423	

[4] Samples were analyzed after the 28 day holding period

Table A22: Bromide analysis #5 ozone effluent sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
22	F 12/13/2012	1/29/2013	0.0681	[4]
26	F 12/17/2012	1/29/2013	0.0536	[4]
28	F 12/29/2012	1/29/2013	0.0904	[4]
30	F1/4/2013	1/29/2013	0.0485	

[4] Samples were analyzed after the 28 day holding period

Table A23: Bromide analysis #5 groundwater sample concentrations

#	Sample	Analysis Date	Bromide (ppm)	Notes
31	WELL 6	1/30/2013	0.2758	[4]
32	WELL 8 11/30/2012	1/30/2013	0.0563	[4]
34	WELL 9 11/30/2012	1/30/2013	0.07	[4]
35	WELL 2 11/2/2012	1/30/2013	0.0332	[4]
36	WELL 1 11/2/2012	1/30/2013	0.0371	[4]

[4] Samples were analyzed after the 28 day holding period

Table A24: Bromate analysis #1 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovery/Difference	
				%	Requirement
1	Blank	n.a.	0	n.a.	≤ 1/3 MRL
2	0.25 ppb	0.227	0.25	90.80	50 % to 150 %
3	0.50 ppb	0.553	0.5	110.60	50 % to 150 %
4	1.00 ppb	1.04	1	104.00	80 % to 120 %
5	2.50 ppb	2.367	2.5	94.68	80 % to 120 %
6	5.00 ppb	4.928	5	98.56	80 % to 120 %
7	10.00 ppb	10.315	10	103.15	80 % to 120 %
8	15.00 ppb	14.846	15	98.97	80 % to 120 %
9	Blank	n.a.	0	n.a.	≤ 1/3 MRL
10	0.25 ppb CCC	0.226	0.25	90.40	50 % to 150 %
11	LSSM	n.a.	n.a.	n.a.	n.a.
12	LFSSM (20 ppb)	20.389	20	101.95	80 % to 120 %
13	Blank	n.a.	0	n.a.	≤ 1/3 MRL
16	9/2/2012 D FORT	8.073	8.356	85.85	80 % to 120 %
17	9/2/2012 D DUP	6.356	6.704	-5.33	± 20 %
26	CCC (5.00PPB)	4.385	5	87.70	80 % to 120 %
37	CCC (15PPB)	12.621	15	84.14	80 % to 120 %
40	9/25/2012 B FORT	2.263	1.268	99.75	80 % to 120 %
41	9/25/2012 B DUP	0.268	0.39	-37.08	± 50 %
50	CCC (2.5 PPB)	1.803	2.5	72.12	80 % to 120 %

Table A25: Bromate analysis #1 Section 1 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
14	9/2/2012 B	9/27/2012	1.109
19	9/4/2012 B	9/28/2012	1.566
22	9/6/2012 B	9/28/2012	1.939
25	9/11/2012 B	9/28/2012	0.59
29	9/13/2012 B	9/28/2012	0.245[2]
32	9/16/2012 B	9/28/2012	n.d.
35	9/22/2012 B	9/28/2012	0.467
39	9/25/2012 B	9/28/2012	0.390[1]
44	8/11/2012 B	9/28/2012	1.228[1,4]
47	8/12/2012 B	9/29/2012	1.947[1,4]

Table A26: Bromate analysis #1 Section 2 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
15	9/2/2012 D	9/28/2012	6.704
20	9/4/2012 D	9/28/2012	3.956
23	9/6/2012 D	9/28/2012	6.882
27	9/11/2012 D	9/28/2012	1.754
30	9/13/2012 D	9/28/2012	1.806
33	9/16/2012 D	9/28/2012	1.658
36	9/22/2012 D	9/28/2012	1.302
42	9/25/2012 D	9/28/2012	1.433[1]
45	8/11/2012 D	9/28/2012	5.380[1,4]
48	8/12/2012 D	9/29/2012	4.626[1,4]

Table A27: Bromate analysis #1 Section 3 sample concentrations

Injection #	Sample Description	Analysis Date	Bromate (ppb)
18	9/2/2012 F	9/28/2012	10.344
21	9/4/2012 F	9/28/2012	8.458
24	9/6/2012 F	9/28/2012	10.775
28	9/11/2012 F	9/28/2012	3.484
31	9/13/2012 F	9/28/2012	2.887
34	9/16/2012 F	9/28/2012	3.695
38	9/22/2012 F	9/28/2012	3.131[1]
43	9/25/2012 F	9/28/2012	3.458[1]
46	8/11/2012 F	9/29/2012	8.361[1,4]
49	8/12/2012 F	9/29/2012	7.552[1,4]

[1] Samples were analyzed outside of the proper recovery for CCC standards

[4] Samples were analyzed after the 28 day holding period

Table A28: Bromate analysis #2 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovery/Difference %	Recovery/Difference Requirement
9	Blank	n.a.	0		≤ 1/3 MRL
10	0.25 ppb CCC	n.a.	0.25	0.00	50 % to 150 %
11	LSSM	n.a.	n.a.	n.a.	n.a.
12	LFSSM (15 ppb)	20.114	20	100.57	80 % to 120 %
13	LFB (1.00 ppb)	0.662	1	66.20	50 % to 150 %
24	CCC (10 PPB)	8.089	10	80.89	80 % to 120 %
27	7/19/2012 D FORT	3.492	3.807	84.25	50 % to 150 %
28	7/19/2012 D DUP	1.396	1.807	-25.66	± 50 %
31	LFB (1 ppb)	0.545	1	54.50	50 % to 150 %
38	CCC (5 PPB)	4.135	5	82.70	80 % to 120 %
49	CCC (10 PPB)	7.938	10	79.38	80 % to 120 %
52	8/14/2012 D FORT	3.973	4.014	97.95	50 % to 150 %
53	8/14/2012 D DUP	1.818	2.014	-10.23	± 50 %
62	CCC (2.5 PPB)	1.683	2.5	67.32	80 % to 120 %
73	CCC (15 PPB)	11.783	15	78.55	80 % to 120 %
76	7/3/2012 F FORT	16.232	16.496	86.80	50 % to 150 %
77	7/3/2012 F DUP	14.35	14.496	-1.01	± 20 %
81	Blank	n.a.	0		≤ 1/3 MRL
87	CCC (2.5 PPB)	2.082	2.5	83.28	80 % to 120 %
98	CCC (10 PPB)	8.787	10	87.87	80 % to 120 %
101	6/19/2012 F CHECK FORT	13.339	13.689	82.50	50 % to 150 %
102	6/19/2012 F CHECK DUP	12.005	11.689	2.67	± 20 %
111	CCC (5 PPB)	4.167	5	83.34	80 % to 120 %
122	CCC (15 PPB)	12.982	15	86.55	80 % to 120 %
125	8/28/2012 B FORT	3.207	3.551	82.80	50 % to 150 %
126	8/28/2012 B DUP	1.362	1.551	-12.98	± 50 %
135	CCC (2.5 PPB)	2.035	2.5	81.40	80 % to 120 %
146	CCC (10 PPB)	9.037	10	90.37	80 % to 120 %
149	7/2/2012 B FORT	3.721	3.836	94.25	50 % to 150 %
150	7/2/2012 B DUP	1.647	1.836	-10.85	± 50 %
159	CCC (5 PPB)	4.575	5	91.50	80 % to 120 %
170	CCC (15 PPB)	13.444	15	89.63	80 % to 120 %
173	7/26/2012 F FORT	8.353	9.081	63.60	50 % to 150 %
174	7/26/2012 F DUP	6.821	7.081	-3.74	± 20 %
183	CCC (2.5 PPB)	2.299	2.5	91.96	80 % to 120 %
194	CCC (10 PPB)	9.417	10	94.17	80 % to 120 %
197	10/7/2012 D FORT	4.784	5.222	78.10	50 % to 150 %

Table A28: Bromate analysis #2 quality control (continued)

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovery/Difference	
				%	Requirement
198	10/7/2012 D DUP	3.287	3.222	2.00	± 20 %
207	CCC (5 PPB)	4.594	5	91.88	80 % to 120 %
218	CCC (15 PPB)	14.379	15	95.86	80 % to 120 %
221	6/26/2012 B FORT	5.958	6.107	92.55	50 % to 150 %
222	6/26/2012 B DUP	3.773	4.107	-8.48	± 20 %
231	CCC (2.5 PPB)	2.108	2.5	84.32	80 % to 120 %
242	CCC (10 PPB)	9.712	10	97.12	80 % to 120 %
245	6/27/2012 F1 FORT	19.166	19.88	64.30	50 % to 150 %
246	6/27/2012 F1 DUP	20.132	17.88	11.85	± 20 %
253	0.50 ppb	0.46	0.5	92.00	50 % to 150 %
254	0.25 ppb	0.165	0.25	66.00	50 % to 150 %
256	CCC (1.00 ppb)	0.716	1	71.60	50 % to 150 %
257	Blank	n.a.	0		≤ 1/3 MRL

Table A29: Bromate analysis #2 Section 1 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
39	6/29/2012 B	10/2/2012	4.619[1,4]
42	7/29/2012 B	10/2/2012	1.442[1,4]
46	8/1/2012 B	10/3/2012	1.062[1,4]
50	8/14/2012 B	10/3/2012	1.62[1,4]
55	9/27/2012 B	10/3/2012	1.169[1]
58	10/2/2012 B	10/3/2012	n.d. [1]
63	9/25/2012 B	10/3/2012	0.339[1,2]
66	8/11/2012 B	10/3/2012	0.934[1,2,4]
69	8/12/2012 B	10/3/2012	2.014[1,4]
72	7/3/2012 B	10/3/2012	4.547[1,4]
78	7/6/2012 B	10/4/2012	7.973[1,4]
92	5/29/2012 B	10/4/2012	5.676[4]
95	6/4/2012 B	10/4/2012	5.056[4]
109	7/22/2012 B	10/5/2012	0.999[2,4]
113	7/23/2012 B	10/5/2012	0.85[2,4]
116	8/7/2012 B	10/5/2012	0.647[2,4]
119	10/4/2012 B	10/5/2012	0.479[2]
124	8/28/2012 B	10/5/2012	1.551[4]
128	8/19/2012 B	10/5/2012	n.d.[4]
131	8/16/2012 B	10/5/2012	0.72[2,4]
134	7/14/2012 B	10/6/2012	n.d.[4]

Table A29: Bromate analysis #2 Section 1 sample concentrations (continued)

#	Sample	Analysis Date	Bromate (ppb)
138	7/13/2012 B	10/6/2012	1.98[4]
141	7/12/2012 B	10/6/2012	1.689[4]
144	7/10/2012 B	10/6/2012	7.405[4]
148	7/2/2012 B	10/6/2012	1.836[4]
153	7/1/2012 B	10/6/2012	4.816[4]
156	8/24/2012 B	10/7/2012	1.357[4]
160	8/22/2012 B	10/7/2012	1.059[4]
163	8/13/2012 B	10/7/2012	0.903[2,4]
166	8/6/2012 B	10/7/2012	1.035[4]
169	7/26/2012 B	10/7/2012	2.459[4]
175	7/24/2012 B	10/7/2012	1.089[4]
178	7/21/2012 B	10/7/2012	0.563[2,4]
181	7/20/2012 B	10/7/2012	0.589[2,4]
185	7/18/2012 B	10/7/2012	n.d.[4]
188	7/17/2012 B	10/8/2012	0.63[2,4]
191	7/5/2012 B	10/8/2012	9.078[4]
195	10/7/2012 B	10/8/2012	0.646[2]
200	6/21/2012 B	10/8/2012	1.79[4]
203	6/20/2012 B	10/8/2012	1.95[4]
206	6/18/2012 B	10/8/2012	4.746[4]
210	6/17/2012 B	10/8/2012	8.942[4]
213	6/16/2012 B	10/8/2012	8.408[4]
216	6/27/2012 B2	10/9/2012	2.55[4]
220	6/26/2012 B	10/9/2012	4.107[4]
225	6/23/2012 B	10/9/2012	1.49[4]
228	6/13/2012 B	10/9/2012	2.76[4]
232	6/12/2012 B	10/9/2012	5.05[4]
235	6/8/2012 B	10/9/2012	5.381[4]
238	6/6/2012 B	10/9/2012	7.678[4]
241	6/27/2012 B1	10/9/2012	4.097[4]
247	6/3/2012 B	10/10/2012	2.918_4
249	6/2/2012 B	10/10/2012	2.737[4]
251	6/1/2012 B	10/10/2012	1.937[4]

[1] Samples were analyzed outside of the proper recovery for CCC standards

[2] Sample concentrations were less than the MRL

[4] Samples were analyzed after the 28 day holding period

Table A30: Bromate analysis #2 Section 2 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
14	6/5/2012 D	10/2/2012	13.427[4]
15	6/7/2012 D	10/2/2012	6.66[4]
17	6/19/2012 D	10/2/2012	7.984[4]
18	6/22/2012 D	10/2/2012	3.498[4]
19	6/25/2012 D	10/2/2012	5.025[4]
20	6/28/2012 D	10/2/2012	6.928[4]
23	7/11/2012 D	10/2/2012	17.661[3,4]
25	7/15/2012 D	10/2/2012	4.8[4]
26	7/19/2012 D	10/2/2012	1.807[4]
29	7/25/2012 D	10/2/2012	4.111[4]
30	7/31/2012 D	10/2/2012	1.876[4]
32	8/3/2012 D	10/2/2012	20.471[3,4]
33	8/9/2012 D	10/2/2012	1.916[4]
34	8/15/2012 D	10/2/2012	2.824[4]
35	8/20/2012 D	10/2/2012	2.038[4]
36	8/26/2012 D	10/2/2012	2.993[4]
37	8/31/2012 D	10/2/2012	2.034[4]
40	6/29/2012 D	10/2/2012	11.763[1,4]
43	7/29/2012 D	10/2/2012	3.441[1,4]
47	8/1/2012 D	10/3/2012	2.733[1,4]
51	8/14/2012 D	10/3/2012	2.014[1,4]
56	9/27/2012 D	10/3/2012	2.933[1]
59	10/2/2012 D	10/3/2012	0.819[1,2]
64	9/25/2012 D	10/3/2012	1.307[1]
67	8/11/2012 D	10/3/2012	5.305[1,4]
70	8/12/2012 D	10/3/2012	4.541[1,4]
74	7/3/2012 D	10/3/2012	9.417[1,4]
79	7/6/2012 D	10/4/2012	11.202[1,4]
93	5/29/2012 D	10/4/2012	11.475[4]
96	6/4/2012 D	10/4/2012	9.309[4]
99	6/11/2012 D CHECK	10/4/2012	18.229[3,4]
105	7/9/2012 D CHECK	10/5/2012	13.408[4]
107	7/4/2012 D CHECK	10/5/2012	13.242[4]
110	7/22/2012 D	10/5/2012	3.241[4]
114	7/23/2012 D	10/5/2012	2.903[4]
117	8/7/2012 D	10/5/2012	1.857[4]
120	10/4/2012 D	10/5/2012	2.112
123	8/28/2012 D	10/5/2012	4.125[4]
129	8/19/2012 D	10/5/2012	1.386[4]
132	8/16/2012 D	10/6/2012	1.763[4]
136	7/14/2012 D	10/6/2012	5.052[4]

Table A30: Bromate analysis #2 Section 2 sample concentrations (continued)

#	Sample	Analysis Date	Bromate (ppb)
139	7/13/2012 D	10/6/2012	6.782[4]
142	7/12/2012 D	10/6/2012	6.072[4]
145	7/10/2012 D	10/6/2012	13.784[4]
151	7/2/2012 D	10/6/2012	4.656[4]
154	7/1/2012 D	10/6/2012	9.981[4]
157	8/24/2012 D	10/7/2012	2.049[4]
161	8/22/2012 D	10/7/2012	1.36[4]
164	8/13/2012 D	10/7/2012	2.989[4]
167	8/6/2012 D	10/7/2012	3.547[4]
171	7/26/2012 D	10/7/2012	3.896[4]
176	7/24/2012 D	10/7/2012	2.816[4]
179	7/21/2012 D	10/7/2012	1.615[4]
182	7/20/2012 D	10/7/2012	2.393[4]
186	7/18/2012 D	10/8/2012	2.106[4]
189	7/17/2012 D	10/8/2012	1.559[4]
192	7/5/2012 D	10/8/2012	18.358[3,4]
196	10/7/2012 D	10/8/2012	3.222[4]
201	6/21/2012 D	10/8/2012	4.224[4]
204	6/20/2012 D	10/8/2012	5.297[4]
208	6/18/2012 D	10/8/2012	13.235[4]
211	6/17/2012 D	10/8/2012	15.554[3,4]
214	6/16/2012 D	10/8/2012	14.583[4]
217	6/27/2012 D2	10/9/2012	6.419[4]
223	6/26/2012 D	10/9/2012	11.326[4]
226	6/23/2012 D	10/9/2012	5.164[4]
229	6/13/2012 D	10/9/2012	7.726[4]
233	6/12/2012 D	10/9/2012	15.469[3,4]
236	6/8/2012 D	10/9/2012	11.255[4]
239	6/6/2012 D	10/9/2012	15.463[3,4]
243	6/27/2012 D1	10/9/2012	10.417[4]

[1] Samples were analyzed outside of the proper recovery for CCC standards

[2] Sample concentrations were less than the MRL

[3] Sample concentrations were greater than the highest calibration standard

[4] Samples were analyzed after the 28 day holding period

Table A31: Bromate analysis #2 Section 3 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
44	7/29/2012 F	10/3/2012	6.327[1,4]
48	8/1/2012 F	10/3/2012	4.346[1,4]
54	8/14/2012 F	10/3/2012	4.5[1,4]
57	9/27/2012 F	10/3/2012	4.833[1]
60	10/2/2012 F	10/3/2012	2.412[1]
61	9/22/2012 F	10/3/2012	2.565[1]
65	9/25/2012 F	10/3/2012	3.06[1]
68	8/11/2012 F	10/3/2012	8.028[1,4]
71	8/12/2012 F	10/3/2012	7.331[1,4]
75	7/3/2012 F	10/4/2012	14.496[1,4]
80	7/6/2012 F	10/4/2012	21.343[1,3,4]
94	5/29/2012 F	10/4/2012	18.963[3,4]
97	6/4/2012 F	10/4/2012	13.53[4]
100	6/19/2012 F CHECK	10/4/2012	11.689[4]
103	6/28/2012 F CHECK	10/5/2012	11.614[4]
104	6/29/2012 F CHECK	10/5/2012	18.914[3,4]
106	7/11/2012 F CHECK	10/5/2012	25.347[3,4]
108	8/3/2012 F CHECK	10/5/2012	27.803[3,4]
112	7/22/2012 F	10/5/2012	5.291[4]
115	7/23/2012 F	10/5/2012	5.25[4]
118	8/7/2012 F	10/5/2012	4.667[4]
121	10/4/2012 F	10/5/2012	4.022
127	8/28/2012 F	10/5/2012	6.629[4]
130	8/19/2012 F	10/5/2012	3.953[4]
133	8/16/2012 F	10/6/2012	3.001[4]
137	7/14/2012 F	10/6/2012	7.918[4]
140	7/13/2012 F	10/6/2012	10.463[4]
143	7/12/2012 F	10/6/2012	10.43[4]
147	7/10/2012 F	10/6/2012	22.48[3,4]
152	7/2/2012 F	10/6/2012	8.362[4]
155	7/1/2012 F	10/6/2012	17.1[4]
158	8/24/2012 F	10/7/2012	4.637[4]
162	8/22/2012 F	10/7/2012	3.657[4]
165	8/13/2012 F	10/7/2012	5.299[4]
168	8/6/2012 F	10/7/2012	6.1[4]
172	7/26/2012 F	10/7/2012	7.081[4]
177	7/24/2012 F	10/7/2012	4.715[4]
180	7/21/2012 F	10/7/2012	3.916[4]
184	7/20/2012 F	10/7/2012	4.435[4]
187	7/18/2012 F	10/8/2012	5.24[4]
190	7/17/2012 F	10/8/2012	2.254[4]

Table A31: Bromate analysis #2 Section 3 sample concentrations (continued)

#	Sample	Analysis Date	Bromate (ppb)
193	7/5/2012 F	10/8/2012	24.063[3,4]
199	10/7/2012 F	10/8/2012	6.302
202	6/21/2012 F	10/8/2012	9.749[4]
205	6/20/2012 F	10/8/2012	8.833[4]
209	6/18/2012 F	10/8/2012	25.522[3,4]
212	6/17/2012 F	10/8/2012	22.946[3,4]
215	6/16/2012 F	10/8/2012	22.733[3,4]
219	6/27/2012 F2	10/9/2012	13.112[4]
224	6/26/2012 F	10/9/2012	16.327[3,4]
227	6/23/2012 F	10/9/2012	9.609[4]
230	6/13/2012 F	10/9/2012	13.679[4]
234	6/12/2012 F	10/9/2012	23.124[3,4]
237	6/8/2012 F	10/9/2012	15.789[3,4]
240	6/6/2012 F	10/9/2012	21.435[3,4]
244	6/27/2012 F1	10/9/2012	17.88[3,4]
248	6/3/2012 F	10/10/2012	10.904[4]
250	6/2/2012 F	10/10/2012	11.333[4]
252	6/1/2012 F	10/10/2012	8.954[4]

[1] Samples were analyzed outside of the proper recovery for CCC standards

[2] Sample concentrations were less than the MRL

[3] Sample concentrations were greater than the highest calibration standard

[4] Samples were analyzed after the 28 day holding period

Table A32: Bromate analysis #3 quality control

#	Sample	Measured (ppm)	Theoretical (ppm)	Recovery/Difference	
				%	Requirement
1	Blank	n.a.	0.000	n.a.	≤ 1/3 MRL
2	Blank	n.a.	0.000	n.a.	≤ 1/3 MRL
3	0.25 ppb	n.a.	0.250	0.00	50 % to 150 %
4	0.50 ppb	0.527	0.500	105.40	50 % to 150 %
5	1.00 ppb	0.868	1.000	86.80	50 % to 150 %
6	2.50 ppb	2.341	2.500	93.64	80 % to 120 %
7	5.00 ppb	4.630	5.000	92.60	80 % to 120 %
8	10.0 ppb	9.762	10.000	97.62	80 % to 120 %
9	15.0 ppb	15.314	15.000	102.09	80 % to 120 %
10	Blank	n.a.	0.000	n.a.	≤ 1/3 MRL
11	Blank	n.a.	0.000	n.a.	≤ 1/3 MRL
12	CCC (0.5 PPB)	0.466	0.500	93.20	50 % to 150 %
13	LFB	0.965	1.000	96.50	50 % to 150 %
16	0.500 ppb CCC	0.561	0.500	112.20	50 % to 150 %
17	0.25 ppb CCC	n.a.	0.250	0.00	50 % to 150 %
18	D FORT 10/9/2012	1.484	1.779	70.50	50 % to 150 %
19	D DUP 10/9/2012	0.779	0.848	-8.48	± 50 %
28	CCC (2.5 PPB)	2.353	2.500	94.12	80 % to 120 %
39	CCC (15 PPB)	14.999	15.000	99.99	80 % to 120 %
42	B FORT 11/7/2012	0.783	1.000	78.30	50 % to 150 %
43	B DUP 11/7/2012	n.a.	0.000	0.00	± 50 %
52	CCC (5 PPB)	4.464	5.000	89.28	80 % to 120 %
59	BLANK	n.a.	0.000	n.a.	≤ 1/3 MRL
60	CCC (0.5 PPB)	0.491	0.500	98.20	50 % to 150 %
61	BLANK	n.a.	0.000	n.a.	≤ 1/3 MRL

Table A33: Bromate analysis #3 Section 1 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
14	B 10/9/2012	12/19/2012	0.502[4]
21	B 10/16/2012	1/4/2013	n.d.[4]
24	B 10/18/2012	1/4/2013	0.311[2,4]
27	B 10/20/2012	1/4/2013	n.d.[4]
31	B 10/24/2012	1/5/2013	n.d.[4]
34	B 10/26/2012	1/5/2013	n.d.[4]
37	B 10/30/2012	1/5/2013	n.d.[4]
41	B 11/7/2012	1/5/2013	n.d.[4]
46	B 12/13/2012	1/5/2013	0.398[2]
49	B 12/17/2012	1/5/2013	n.d.
53	B 12/29/2012	1/5/2013	0.3[2]
56	B 1/4/2013	1/5/2013	n.d.

[2] Sample concentrations were less than the MRL
[4] Samples were analyzed after the 28 day holding period

Table A34: Bromate analysis #3 Section 2 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
15	D 10/9/2012	12/19/2012	0.848[4]
22	D 10/16/2012	1/4/2013	0.432[2,4]
25	D 10/18/2012	1/4/2013	0.834[4]
29	D 10/20/2012	1/4/2013	0.741[4]
32	D 10/24/2012	1/4/2013	0.452[2,4]
35	D 10/26/2012	1/4/2013	0.639[4]
38	D 10/30/2012	1/5/2013	n.d.[4]
44	D 11/7/2012	1/5/2013	n.d.[4]
47	D 12/13/2012	1/5/2013	0.691
50	D 12/17/2012	1/5/2013	0.579
54	D 12/29/2012	1/5/2013	0.446[2]
57	D 1/4/2013	1/5/2013	n.d.

[2] Sample concentrations were less than the MRL
[4] Samples were analyzed after the 28 day holding period

Table A35: Bromate analysis #3 Section 3 sample concentrations

#	Sample	Analysis Date	Bromate (ppb)
20	F 10/9/2012	1/4/2013	1.568[4]
23	F 10/16/2012	1/4/2013	1.243[4]
26	F 10/18/2012	1/4/2013	1.362[4]
30	F 10/20/2012	1/5/2013	1.694[4]
33	F 10/24/2012	1/5/2013	1.204[4]
36	F 10/26/2012	1/5/2013	1.280[4]
40	F 10/30/2012	1/5/2013	1.204[4]
45	F 11/7/2012	1/5/2013	2.054[4]
48	F 12/13/2012	1/5/2013	0.766
51	F 12/17/2012	1/5/2013	0.628
55	F 12/29/2012	1/5/2013	n.d.
58	F 1/4/2013	1/5/2013	n.d.

[4] Samples were analyzed after the 28 day holding period