

Evaluation of Bromate Formation and Control using Preformed Monochloramine in
Ozonation for Indirect Potable Reuse

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ACADEMIC ABSTRACT

Ozone can act as a powerful oxidant and disinfectant in treatment for potable reuse. However, bromate, a regulated possible carcinogen, can form as a byproduct and limit the application of ozonation when bromide is present. Bromate is formed through a series of reactions with ozone and hydroxyl radicals, which form through ozone decomposition in water. In pilot-scale testing, preformed monochloramine addition limited bromate formation to below the maximum contaminant level of 10 µg/L at ozone doses up to 6.4 mg/L with bromide concentrations as high as 508 µg/L. Preforming monochloramine in a separate carrier water allowed the mechanisms of bromate suppression to be examined without the effects of chlorine reactions with organic matter present. Monochloramine was shown to be acting as a hydroxyl radical scavenger and reduced estimated hydroxyl radical exposure by as much as 70 percent. Additionally it was hypothesized that bromamine (NH₂Br) was forming from ammonia and hypobromous acid (HOBr), an important intermediate, preventing HOBr from further oxidation to bromate. Increasing ozone dose showed an immediate improvement in total organic carbon (TOC) removal through downstream biofilters and may warrant increasing ozone dose above where disinfection objectives are met. Additional testing showed that the majority of bromate formed in the initial phase of ozonation occurring in the dissolution column where ozone gas is added and no disinfection credit is received. Monochloramine addition reduced bromate formation by as much as 97% and shows promise for ozonation application in high bromide reuse waters where bromate formation is a concern.

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GENERAL ABSTRACT

Ozone is a powerful oxidant and disinfectant used in potable wastewater reuse to destroy specific harmful compounds, including pharmaceuticals, personal care products and endocrine disrupting compounds. Ozonation also increases the biodegradability of recalcitrant organic compounds and inactivates disease-causing microbes. However, bromate, a regulated possible human carcinogen can form when bromide is present due to natural or industrial sources. Pilot-scale testing on wastewater treatment plant effluent with high bromide concentrations showed that the addition of preformed monochloramine could reduce bromate formation by as much as 97%. Monochloramine addition was able to keep concentrations below the U.S. Environmental Protection Agency Maximum Contaminant Level of 10 µg/L while exceeding 3-log or 99.9% virus removal credit. Preforming monochloramine in separate carrier water prior to addition upstream of ozonation eliminated the potential for disinfection byproduct formation when monochloramine is formed in the main water flow. This also allowed for the mechanisms of bromate suppression by monochloramine to be examined without the influence of reactions between chlorine and dissolved organic matter present. This research can help increase the application of ozonation in water reuse.

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1 Introduction

Population growth and climate change have led to increasing water scarcity and generated greater interest in wastewater reuse. Membrane based treatment processes have traditionally been used for direct and indirect potable reuse scenarios. However, these systems are often prohibitively expensive and create concentrated brine streams which are difficult to dispose of, especially for inland communities. Recently “carbon based” treatment trains involving ozonation coupled with biologically activated carbon filtration have gained popularity. In these systems ozone oxidizes dissolved organic matter (DOM) and trace organic contaminants (TOxCs) including pharmaceuticals, personal care products, and endocrine disrupting compounds into more biodegradable transformation products. Ozone is also a powerful disinfectant and can serve as a barrier against pathogen transmission.

Bromate is a potential human carcinogen formed through the ozonation of bromide containing waters. Bromate is created through reactions with both ozone and hydroxyl radicals which are formed as a secondary oxidant through the decomposition of ozone in water. Bromate is the only regulated disinfection byproduct of ozonation with a maximum contaminant level (MCL) of 10 µg/L. Formation and control of bromate have been studied extensively in natural source waters for drinking water treatment. However, how this applies in wastewater reuse is still not entirely understood. There is currently no regulation for bromate formation for wastewater treatment plants that use ozone for disinfection. In reuse applications ozone doses and hydroxyl radical exposures are often much higher than those used in drinking water treatment. Additionally, higher bromide concentrations are often present from salt water infiltration and industrial sources so controlling bromate formation is critical.

Several bromate control strategies have been developed in order to meet the MCL. pH suppression shifts the equilibrium of the key intermediate hypobromous acid, HOBr, and decreases hydroxyl radical generation. Ammonia addition masks HOBr as monobromamine, NH₂Br, and prevents its further oxidation towards bromate. Monochloramine based strategies include the chlorine-ammonia process, which forms and masks HOBr and NH₂Br prior to

ozonation and $\text{NH}_3\text{-Cl}_2$ which forms monochloramine to act as a hydroxyl radical scavenger and possibly mask HOBr as well.

1.1 Project Motivation and Objectives

Ozonation is an integral part of the indirect potable reuse treatment process in Hampton Roads Sanitation District's (HRSD) Sustainable Water Initiative for Tomorrow (SWIFT). The advanced treatment train consists of coagulation, flocculation, sedimentation, ozonation, biofiltration, granular activated carbon adsorption, and UV disinfection prior to injection into the Potomac Aquifer while meeting all primary drinking water MCLs. Pilot testing of the treatment process began at HRSD's York River Treatment Plant in June 2016. A 1 million gallon per day (MGD) demonstration facility and research center was completed in May 2018 with the intention of full scale implementation at five treatment plants totaling 100 MGD by 2030.

In this process ozone is used to oxidize trace organic compounds and bulk organic material for assimilable organic carbon (AOC) generation for biofiltration. At the SWIFT Research Center, ozone is also required to provide at least 3-log virus inactivation credit as one of multiple barriers against pathogens. Bromate formation was recognized as a major concern early in pilot testing, ammonia addition was not able to suppress bromate formation and pH depression was deemed impractical due to the high alkalinity. Average bromide concentrations at York River Treatment Plant were around 400 $\mu\text{g/L}$ while other HRSD treatment plants see bromide concentrations of 1.3 mg/L or higher.

Preformed monochloramine was selected to control bromate formation. In this setup chlorine and then ammonia are added to a separate carrier water to form monochloramine prior to addition to the bulk flow. This eliminates the disinfection byproduct formation and chemical demand associated with free chlorination in the $\text{Cl}_2\text{-NH}_3$ process and the possibility of NDMA formation from dichloramines due to improper mixing with in-situ formation of monochloramine. Chapter 2 reviews some of the previous literature on ozonation in wastewater and reuse and looks at what is known about chlorine and ammonia based bromate control strategies.

In Chapter 3, monochloramine addition for bromate control is evaluated on the pilot scale. Bromate formation was controlled to below the MCL with monochloramine addition. The implications of monochloramine on treatment performance including advanced oxidation and ozone exposure and disinfection credit are evaluated. While the aim of this study was not to determine the mechanisms of bromate suppression by monochloramine, important conclusions about intermediate formation and radical scavenging can be drawn.

With the upcoming implementation of full scale ozone based reuse treatment plants, both at HRSD and elsewhere, contactor design must be evaluated carefully. Chapter 4 explores considerations for different ozone dissolution systems and contactor designs for bromate formation and control in a reuse scenario.

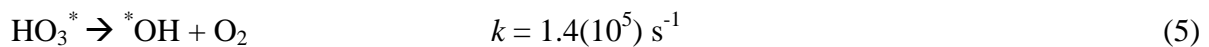
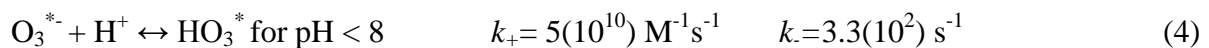
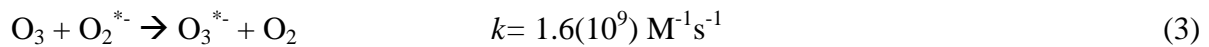
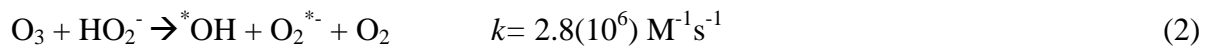
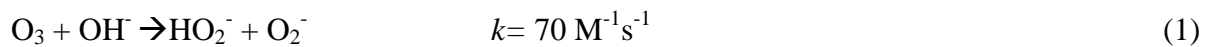
2 Literature Review

2.1 Ozonation in Water Reuse

In water reuse applications, ozone is used to oxidize specific trace organic contaminants (TOrcs) or micropollutants, increase biodegradability, and act as a barrier against pathogens (Gerrity et al., 2011, 2014). TOrcs include pharmaceuticals and personal care products, endocrine disrupting compounds, and other contaminants of emerging concern. Full mineralization of these compounds is not feasible; however, ozone and hydroxyl radicals can destroy the parts of these compounds responsible for their toxicity and convert them into more biodegradable transformation products. For this reason, ozone is often coupled with biological filtration. Assimilable organic carbon (AOC) or biodegradable organic carbon (BDOC) is formed from the ozonation of the bulk dissolved organic matter as well (Knopp et al., 2016; Reungoat et al., 2011, 2012; Wert et al., 2007)

2.2 Ozone Decomposition in Wastewater

Ozone decomposes to form hydroxyl radicals as a secondary oxidant through reactions with dissolved organic matter and autocatalytically. In natural water sources ozone reacts quickly with DOM in the initial phase of 20-30 seconds creating higher *OH concentrations through Reaction 6. This rapid ozone consumption is often referred to as instantaneous decay. In the second phase, ozone decomposition and radical generation then become controlled by Reactions 1 and 7. In this phase R_{ct} , or the ratio of hydroxyl radical exposure to ozone exposure is constant. In the second phase, ozone decay can be modeled as pseudo-first order (Elovitz & Von Gunten, 1999; von Gunten, 2003a).



In the ozonation of wastewater effluent, the reactions with DOM become much more important and there are less distinct phases of ozone decay. Using a quench flow module, Buffle et al. (2006) showed that ozone decay rate continued to change throughout all of ozonation in wastewater and R_{ct} did not become constant. In the first second of decay, *OH concentrations 100 times greater than those seen in advanced oxidation processes (UV/H₂O₂) in natural water were observed, as such wastewater ozonation should be considered an advanced oxidation process. DOM concentrations in wastewater are higher and have higher reactivity towards ozone and hydroxyl radicals. At ozone doses up to 4 mg/L, the addition of a radical scavenger (t-butanol) had minimal impact on ozone decomposition indicating that ozone decay and radical generation are primarily through Reaction 6 throughout time and not just in the initial phase. At higher ozone doses, once the most reactive DOM moieties have been consumed, Reaction 7 may play a larger role (Lee & von Gunten, 2016). The rate constant for Reaction 1 is relatively small and does not control ozone decomposition in wastewater. Increasing decay rates at higher pH are likely due to the increased reactivity of deprotonated DOM species (Buffle et al., 2006).



2.3 Ozone and Hydroxyl Radical Exposure

Ozone exposure is calculated as the ozone concentration integrated over time in mg/L*min or M*s. Similarly *OH exposure is the integral of the hydroxyl radical concentration over time. Because *OH concentrations are difficult to measure directly, a probe compound such as parachlorobenzoic acid (pCBA), which is only degraded by hydroxyl radicals, is used to measure *OH exposure. Due to the nature of the second order rate reactions involved in ozonation, the oxidation of a compound, P, can be calculated by the equation below.

$$-\ln\left(\frac{P}{P_0}\right) = k_{*OH} * \int [^*OH]dt + k_{O_3} * \int [O_3]dt \quad (9)$$

In the second phase of ozonation of natural water the ratio of *OH exposure to O_3 exposure, R_{ct} remains constant. Because of this, kinetic sampling for the oxidation of a compound or the formation of a byproduct, such as bromate, is often compared to ozone exposure rather than just time (Elovitz and von Gunten 1999; von Gunten 2003). Buffle et al. (2006) showed that R_{ct} was not constant in the second phase of wastewater ozonation. However, hydroxyl radical exposure was the same when compared to ozone exposure for multiple ozone doses.

2.4 O_3 :TOC Ratio

Mass based specific ozone doses, which compare ozone dose in mg/L to TOC in mg/L, are often used in wastewater ozonation and for potable reuse to compare doses and treatment performance between plants. Buffle et al. (2006) saw similar ozone decay rates in testing when two municipal wastewater effluents were diluted to the same TOC. Further work has shown that reduction in UV absorbance, hydroxyl radical exposure, and micro-pollutant oxidation are similar across multiple wastewaters when compared on a O_3 :TOC basis (Gerrity et al., 2012; Lee and von Gunten 2016; Chys et al., 2017). There are some exceptions to this as the makeup of the organic carbon is determined by the nature of the influent and the biological process employed. In these cases dosing based on O_3 :TOC can show the relative reactivity of the organics (Wert, Rosario-Ortiz et al., 2007). Typical specific ozone doses are around 1.0 in reuse applications (Lee & von Gunten, 2016)

Nitrite is quickly oxidized by ozone to form nitrate (Liu et al., 2001; Naumov et al., 2010) and consumes 3.43 mg O_3 per mg NO_2^- -N. Due to fluctuations in effluent nitrite in wastewater effluent, specific ozone doses should be corrected for nitrite demand (Lee and von Gunten 2016).

2.5 Change in UV Absorbance, *OH exposure, and micropollutant oxidation

Hydroxyl radical exposure has been correlated with the percent change in UV absorbance at 254 nm. Absorbance changes were calibrated to the probe compound pCBA which is destroyed by hydroxyl radicals but does not react with ozone. These correlations hold up well across multiple wastewater effluents (Chys et al., 2017; Gerrity et al., 2012; Wert et al., 2009b). Micropollutant oxidation can also be predicted due to the good correlation between change in UV and *OH

exposure. UV 254 absorbance is also associated with double bonds and aromatic systems which also react with ozone. There is minimal or no $^{\bullet}\text{OH}$ exposure up to 20% change in UV absorbance which is attributed to direct reactions with ozone. Compounds with high reaction rates with ozone ($k > 10^4 \text{ M}^{-1} \text{ s}^{-1}$) are removed in this range. Despite their high reactivity with $^{\bullet}\text{OH}$ ($k > 10^9 \text{ M}^{-1} \text{ s}^{-1}$), these compounds are nearly entirely oxidized by ozone due to the relative concentrations of ozone and hydroxyl radicals (Buffle et al., 2006; Chys et al., 2017; Wert et al., 2009b).

2.6 Bromate

Bromate was reported as a Group 2B contaminant or possible human carcinogen by the World Health Organization. Tests on mice and rats with potassium bromate lead to the development of renal tumors (Kurokawa et al., 1986). A limit of 3 $\mu\text{g/L}$ was calculated for a 10^{-5} excess lifetime cancer risk. However, a provisional guideline of 25 $\mu\text{g/L}$ was recommended due to the limitations in analytical methods and treatment techniques at the time (WHO, 1993). Following the WHO report the USEPA imposed a maximum contaminant level (MCL) of 10 $\mu\text{g/L}$ (EPA, 1998).

2.7 Bromate Formation

Bromate is formed during the ozonation of bromide through a complex series of pathways involving both ozone and hydroxyl radicals as illustrated in Figure 1.

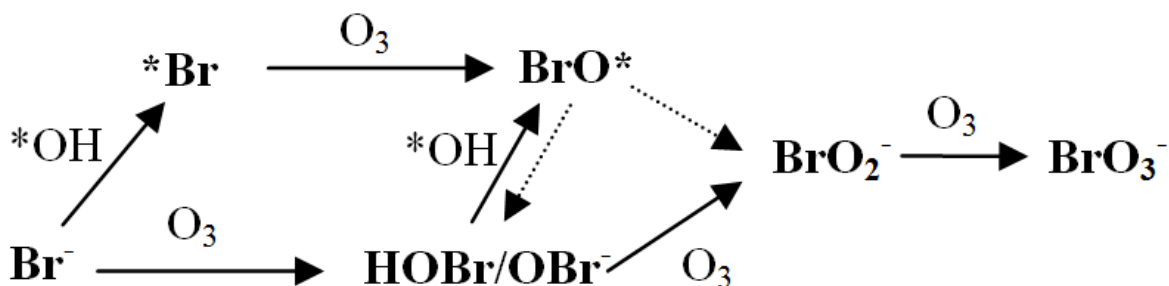


Figure 1. Bromate formation pathways (after Buffle and von Gunten 2004)

In the direct pathway, which consists of only ozone reactions, bromide is oxidized to hypobromous acid or hypobromite (HOBr/OBr^-). The HOBr/OBr^- equilibrium is very important

for the direct pathway, as effectively only OBr^- reacts with ozone to form bromite (BrO_2^-) and then bromate. With a pKa of 9, the amount of OBr^- available for reaction with ozone can vary greatly in the typical pH ranges of water and wastewater treatment (Pinkernell & von Gunten, 2001).

The indirect-direct and direct-indirect pathways consist of both ozone and hydroxyl radical reactions. Bromide is radicalized by hydroxyl radicals and then oxidized to BrO^* by ozone. Hydroxyl radicals form BrO^* from both HOBr and OBr^- , which then disproportionates to BrO_2^- . At high $^*\text{OH}$ concentrations typical to wastewater ozonation, nearly all HOBr/OBr^- reacts with hydroxyl radicals to form $^*\text{BrO}$ (Pinkernell and von Gunten 2001). The final step for bromate formation for all pathways is through molecular ozone.

The direct reactions between bromide and ozone are fairly slow while the hydroxyl radical reactions are extremely fast. However, the relative concentrations of ozone and $^*\text{OH}$ must be taken into account when comparing reaction rates. The majority of HOBr/OBr^- is oxidized by $^*\text{OH}$ during typical drinking water treatment conditions. Nearly 100% of Br^- would be oxidized by $^*\text{OH}$ at the R_{ct} values expected in the initial phase of wastewater ozonation (Pinkernell and von Gunten 2001; Buffle et al. 2006).

2.8 Bromate Control

Bromate formation may become problematic when ozonating water with bromide concentrations greater than 50 $\mu\text{g/L}$ (von Gunten, 2003b). Besides lowering ozone dose, several effective chemical bromate control strategies have been developed and are discussed below.

2.8.1 pH Suppression

pH suppression has been identified as one possible method for controlling bromate formation during ozonation. Decreasing the pH from 8 to 6 can reduce bromate formation by up to 60%. By lowering pH the HOBr/OBr^- equilibrium is shifted toward HOBr , which limits the formation of bromate through the direct pathway. pH suppression also limits the indirect pathways by reducing OH^- which initiates ozone decomposition into hydroxyl radicals.

In natural source waters it is difficult to control the bromate formed in the initial phase through pH depression because hydroxyl radicals are generated through direct reactions with reactive natural organic matter (NOM) and therefore not influenced by the superoxide pathway (Pinkernell and von Gunten 2001). In wastewater, radical generation is predominantly through organic matter for most of ozonation, though protonated species are less reactive and would produce fewer $^{\bullet}\text{OH}$ radicals (Buffle et al. 2006). Bromate formation is more through the indirect pathways so pH suppression may be less effective.

2.8.2 Ammonia Addition

Ammonia addition is a simple method for bromate control. Hypobromous acid reacts with ammonia to form monobromamine, NH_2Br , so the bromide cannot be further oxidized to bromate. Ammonia addition only controls bromate formation through the direct pathway (Pinkernell & von Gunten, 2001).

Bromamine is then slowly oxidized to nitrate and bromide. For this reason ammonia in excess of the stoichiometry for bromamine formation must be added. Pinkernell and von Gunten (2001) found that there was no further decrease in bromate formation past 200 $\mu\text{g/L-N}$ of added ammonia. Wert, Neemann et al. (2007) elaborated that more ammonia could be useful at ozone exposures beyond 10 $\text{mg/L}\cdot\text{min}$ as NH_2Br is oxidized and bromide becomes available again.

2.8.3 Chlorine Ammonia Process

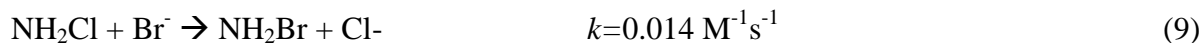
In the $\text{Cl}_2\text{-NH}_3$ process free chlorine is applied upstream of ozonation in order to oxidize Br^- to HOBr . Ammonia is then added in order to mask HOBr as NH_2Br prior to ozonation. Because bromide is not available for oxidation before ozonation, bromate formation is reduced through both the direct and indirect pathways. Free chlorination also serves to reduce initial ozone demand and ozone decay rate by reacting with NOM that would otherwise consume ozone and generate hydroxyl radicals. This allows ozone doses to be lowered to meet disinfection goals,

further reducing bromate formation (Benotti et al., 2011; Buffle et al., 2004; Wert, Neemann, et al., 2007).

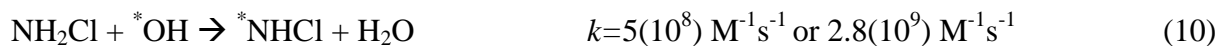
In essence the Cl₂-NH₃ process also consists of monochloramination, as residual free chlorine is often still present upon ammonia addition which forms NH₂Cl prior to ozonation (Buffle et al., 2004).

2.8.4 Monochloramine for Bromate suppression

Monochloramine has been successfully utilized to control bromate formation, though the mechanisms of suppression are not entirely understood (Benotti et al., 2011; Buffle et al., 2004; Ikehata et al., 2013). When ammonia was added upstream of chlorine unexpected bromate reduction was observed by (Buffle et al., 2004) that did not match with the initial model developed for the Cl₂-NH₃ process. Bromamine formation with monochloramine is unlikely as the reaction is very slow.

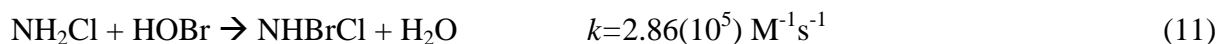


Johnson et al. (2002) and Poskrebyshev et al. (2003) showed that monochloramine acts as a hydroxyl radical scavenger. This would limit the bromate formed through the indirect pathways.



NH₃-Cl₂ or in-situ formed monochloramine reduced hydroxyl radical exposure by more than 50% when compared to ammonia addition only. Some of this may have been due to reactions with free chlorine and nitrogenous NOM which would otherwise react with ozone and generate hydroxyl radicals (Buffle et al., 2004). The rate constant for Equation 10 needs confirmation, the difference of nearly an order of magnitude between the two published rates makes it difficult to separate the effects of radical scavenging by monochloramine and the reduction in $\cdot\text{OH}$ generation due to chlorine reactions with DOM.

The other probable suppression mechanism is the formation of bromochloramine, NHBrCl , which could mask bromide during ozonation (Gazda & Margerum, 1994; Wert, Neemann et al., 2007).



Bromochloramine formation is more than two orders of magnitude slower than bromamine formation, indicating that if this were the only bromate suppression mechanism it would be less effective than ammonia alone. Similar to ammonia addition, NHBrCl formation requires oxidation of bromide to HOBr before masking can occur on a reasonable time scale.

Most of the literature on bromochloramines is in the context of formation in distribution systems with residual monochloramine and bromide i.e. formation over several days (Allard et al., 2018; Luh & Mariñas, 2014). How exactly bromochloramines react with ozone and hydroxyl radicals is yet to be studied.

2.9 Ozone Dissolution Systems

The two primary methods ozone for dissolution are fine bubble diffusion and sidestream injection. Bubble diffusion has been the traditional method of ozone dissolution used in drinking water treatment. In bubble diffusion systems, ozone is added through stone diffusers at the bottom of the contactor. Contactors are typically 18 to 25 feet deep to maximize hydrostatic pressure for efficient gas transfer. The diffusion chamber typically has a 1 to 3 minute detention time. Downstream contact chambers are usually configured in an over-under orientation (Wert et al., 2016).

In sidestream injection systems ozone is added to a portion of the flow by venturi injection and then mixed back into the bulk flow. Sidestream injection systems have become feasible with the improvement in O_3 generators which can generate 8-12% ozone by weight, facilitating higher transfer at lower gas-liquid ratios. These systems are gaining popularity in both new plants and

retrofitting older installations. The primary benefits of sidestream injection are operational; the need for diffuser inspection and maintenance is eliminated. Being removed from the contactor, maintenance on the ozone dissolution equipment does not require confined space entry or draining of tanks. Sidestream injection also reduces the need for deep contactors required for gas transfer in bubble diffusion systems and allows for the use of pipeline contactors. However, sidestream systems are often more expensive to operate due to the increased pumping costs (Rakness, 2007; Rakness et al., 2018; Wert et al., 2016).

In both fine bubble diffusion and sidestream injection systems bromate forms in the dissolution zone before any disinfection credit is earned. When operated at lower flows and longer detention times in the bubble diffusion column, bromate formation as high as 9.1 µg/L was observed by Wert et al. (2017). Ozone exposures sufficient for 19-log virus or 0.5-log *Cryptosporidium* inactivation credit were observed as well. In sidestream systems bromate formed quickly in the sidestream due to the higher ozone dose applied. However, if sidestream detention time was minimized, this bromate formation would be negated in the mixed flow. Direct comparison of bromate formation between sidestream injection and bubble diffusion was not made (Wert et al., 2016, 2017)

3 Manuscript 1- Evaluation of preformed monochloramine for bromate control during ozonation for indirect potable reuse

3.1 ABSTRACT

Bromate forms as a byproduct of the ozonation of bromide through reactions with both ozone and hydroxyl radicals. Bromate formation and control have been studied extensively in natural source waters for drinking water treatment. However, bromate mitigation has not been investigated deeply in wastewater effluents used for potable reuse. In this study preformed monochloramine was evaluated for use as a bromate suppression method in pilot testing of high bromide reuse waters. Bromate was kept below the MCL at ozone doses up to 6.3 mg/L or approximately 1:1 O₃:TOC with 5 mg/L-Cl₂ NH₂Cl at a bromide concentration of 500 µg/L. Monochloramine addition limited bromate formation by as much as 97% when compared to no monochloramine addition. UV absorbance was used as a surrogate for hydroxyl radical exposure and showed that monochloramine appears to act as a hydroxyl radical scavenger and limits bromate formation through the indirect pathways. Monochloramine and excess free ammonia may also be masking HOBr as NH₂Br or NHBrCl to prevent further oxidation to bromate. Ozone decay rate increased with increasing monochloramine dose which may negatively impact disinfection credit.

Keywords: Bromate, Ozonation, Monochloramine, Potable Reuse

3.2 INTRODUCTION AND BACKGROUND

Ozonation coupled with biofiltration has shown promise as an alternative to membrane based processes for direct and indirect potable reuse applications. This process offers significant cost savings in both capital and operating costs as well as eliminating the need to handle concentrated brine streams which are a concern for inland locations (Gerrity et al., 2011, 2014). Hampton Roads Sanitation District's (HRSD) Sustainable Water Initiative for Tomorrow (SWIFT) aims to treat wastewater effluent to drinking water standards to augment the Potomac Aquifer with 100 million gallons per day (MGD) by 2030 to combat land subsidence in eastern Virginia and reduce nutrient loading on the Chesapeake Bay. The treatment train consists of coagulation, flocculation and sedimentation, ozonation, biologically active carbon filtration, and granular

activated carbon followed by UV disinfection. A pilot plant was operated at HRSD's York River Treatment Plant in Seaford, VA to demonstrate the potential of this process before the construction of a 1 MGD Research Center and demonstration facility and eventual full-scale implementation at five treatment plants. In this process ozone provides bulk organics degradation and assimilable organic carbon (AOC) generation and transforms trace organic contaminants (TOrcs) into more readily biodegradable transformation products while providing a barrier against pathogens (Arnold et al., 2018; Knopp et al., 2016; Reungoat et al., 2012; Wert, Rosario-Ortiz, et al. 2007).

Ozone is a powerful oxidant which also leads to the generation of hydroxyl radicals ($^{\bullet}\text{OH}$) through reactions with dissolved organic matter (DOM). Hydroxyl radicals are nonselective and extremely fast reacting. While transient concentrations and exposures are very low, they are considered the strongest oxidant available for water treatment. Ozone decomposition follows multiphasic kinetics. In the initial phase, $t < \sim 30\text{s}$, rapid ozone decomposition takes place due to fast direct reactions with organics that generate large amounts of $^{\bullet}\text{OH}$. After the most reactive DOM has been consumed, the ozone decay rate stabilizes in the second phase and can be approximated by first order decay kinetics (von Gunten 2003a). Due to the higher concentration and reactivity of the organic matter in wastewater effluent, ozonation generates hydroxyl radical concentrations greater than those found in advanced oxidation processes (AOP) in natural waters (Buffle et al., 2006).

Bromate (BrO_3^-) is formed through the ozonation of bromide containing waters. A maximum contaminant level for bromate of $10 \mu\text{g/L}$ was set by the USEPA following a World Health Organization report which classified it as a potential human carcinogen (EPA, 1998; WHO, 1993). Conventional drinking water treatment wisdom states that bromate formation may be an issue if bromide concentrations are greater than $50 \mu\text{g/L}$ (von Gunten, 2003b). Bromate is formed through a complex series of both ozone and hydroxyl radical reactions (Figure 2)(Pinkernell and von Gunten 2001). In the direct pathway ozone oxidizes bromide to hypobromous acid, HOBr . Only OBr^- is then further oxidized by ozone to form BrO_2^- and BrO_3^- . In the direct-indirect pathway HOBr and OBr^- react with hydroxyl radicals to form BrO^{\bullet} which disproportionates to BrO_2^- which is then oxidized to BrO_3^- . The majority of bromate formation

occurs through this pathway during drinking water treatment conditions (Qi et al., 2016; von Gunten, 2003b). The indirect-direct pathway is most important during the initial phase where hydroxyl radical concentrations are highest, bromide is radicalized, reacts with ozone to form BrO^* and then proceeds following the latter half of the direct-indirect pathway (Pinkernell and von Gunten 2001; Qi et al. 2016).

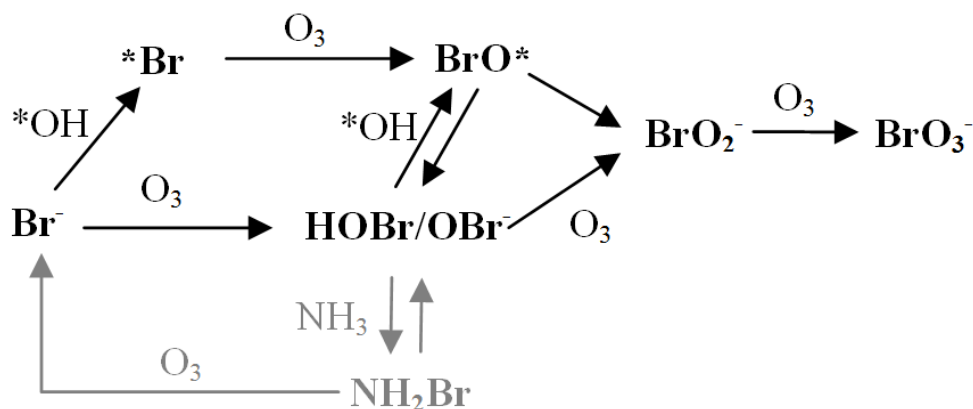


Figure 2- Bromate Formation Pathways (after Pinkernell and von Gunten 2001)

Due to the low lying, coastal nature of HRSD's collection system, bromide concentrations of 400 $\mu\text{g/L}$ or higher are often present due to salt water infiltration as well as specific industrial sources such as landfill leachate. In order to maximize organics degradation and achieve at least 3-log virus inactivation credit while meeting all primary MCLs, controlling bromate formation was vital.

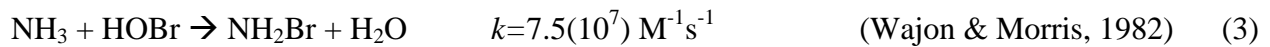
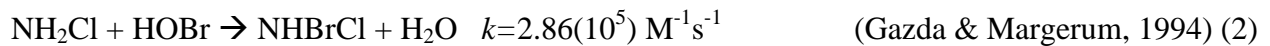
Several common methods exist for suppressing bromate formation. pH depression shifts the HOBr/OBr^- equilibrium toward HOBr , and limits ozone decomposition into hydroxyl radicals. Ammonia addition masks HOBr as bromamine and prevents further oxidation to bromate (Equation 3) (Pinkernell and von Gunten 2001). Due to the high alkalinity of the wastewater effluent, pH suppression was impractical for pilot testing and prohibitively expensive for full scale implementation. Ammonia addition was ineffective; ammonia concentrations in the wastewater effluent were typically high enough for bromamine formation so additional NH_3 had little effect. Preformed monochloramines were chosen for bromate control due to their promising bromate suppression potential without the DBP formation and increased chlorine demand and

chemical usage associated with free chlorination in the Chlorine-Ammonia process (Benotti et al., 2011; Buffle et al., 2004; Wert, Neemann et al., 2007).

The exact mechanisms of bromate suppression by monochloramine are not entirely understood. Monochloramine acts as a hydroxyl radical scavenger (Equation 1) (Johnson et al., 2002; Poskrebyshev, et al., 2003).

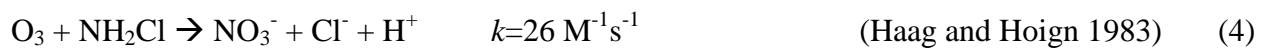


This was hypothesized to be the primary benefit of monochloramine over ammonia addition alone as monochloramine cannot oxidize bromide to HOBr to form NH₂Br before ozonation (Buffle et al., 2004). Monochloramine may also form intermediates to mask hypobromous acid from further oxidation to bromate similar to ammonia (Equation 3). Bromochloramine, NHBrCl, can form from monochloramine and HOBr (Equation 2).



The reaction rates for NHBrCl formation are more than two orders of magnitude slower than bromamine formation so NH₂Br is kinetically favored to form in the presence of free ammonia.

Despite being a radical scavenger, Benotti et al. (2011) found that monochloramine increased ozone decay rate and required a higher ozone dose to achieve the same *Cryptosporidium* inactivation credit. This could be explained in part by monochloramine oxidation by ozone (Equation 4). However, this rate is very slow and may not account for the entirety of the increase in ozone decay.



The objective of this study was to understand the applicability of preformed monochloramine for bromate control in high bromide reuse applications. Pilot tests were conducted in order to better understand the relationships between ozone dose, monochloramine dose and bromate formation. Many of the ozone and monochloramine doses used were much greater than those that have been used in drinking water treatment and previous work. The secondary effects of monochloramine on ozone demand, decay, exposure, and disinfection credit were also analyzed in order to optimize ozonation performance and define an operating range where disinfection objectives were met and bromate formation was controlled. Total organic carbon (TOC) was monitored on the biofilter effluent to see what impact changing ozonation conditions had on biofilter performance. While elucidating the mechanisms of bromate suppression by monochloramine was not the primary objective of this study, observations were analyzed in light of these mechanisms and their practical implications on ozonation.

3.3 MATERIALS AND METHODS

3.3.1 Pilot Setup

A pilot treatment plant consisting of coagulation, flocculation and sedimentation followed by ozonation, biofiltration, granular activated carbon and UV disinfection was operated at HRSD's York River Treatment Plant from June 2016 through May 2018. Figure 3 shows the pilot layout as well as typical operating conditions for the system.

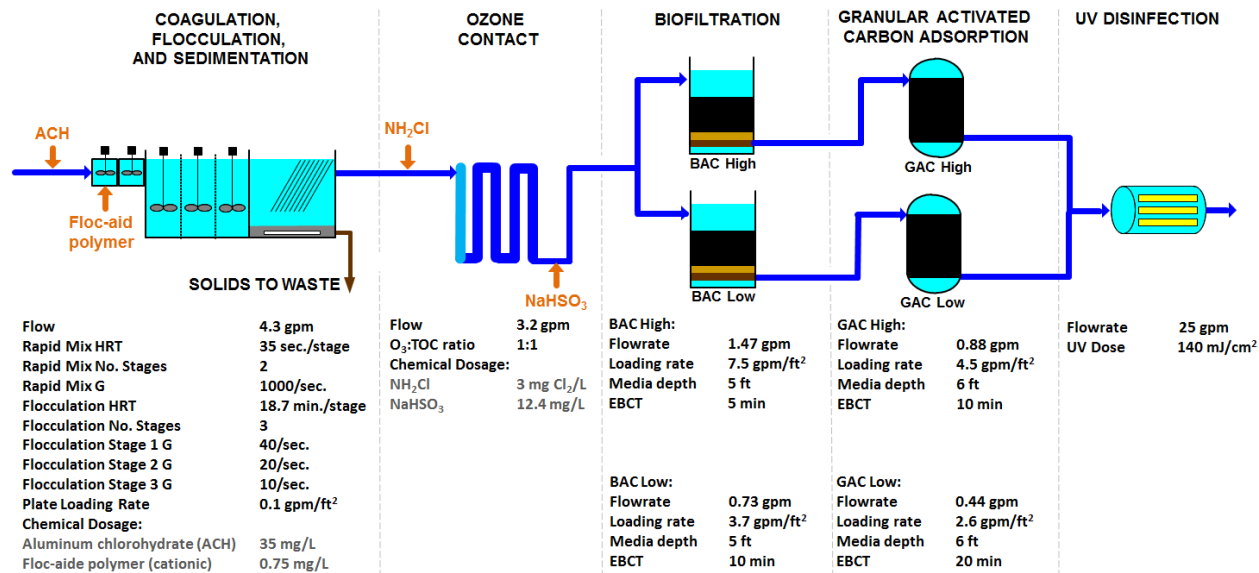


Figure 3- Pilot plant configuration with typical operating parameters

The York River Treatment Plant consists of primary clarification, fully nitrifying conventional activated sludge followed by denitrification filters. The pilot was fed with denitrification filter effluent prior to final disinfection. Due to the low total suspended solids following filtration, mixed liquor was added to the influent to achieve 5 mg/L TSS typical to other plants without filtration. For majority of the testing in this project (from October 2017 to May 2018) a chiller unit was installed upstream of flocculation and sedimentation to lower the temperature to approximately 15° C to simulate winter conditions. Water quality parameters for the ozone influent were fairly stable over the course of testing (Table 1).

Table 1- Water quality parameters during testing

Parameter	TOC	pH	Temperature	Free NH ₃ w/ NH ₂ Cl	Total NH ₃ w/o NH ₂ Cl	Nitrite	Nitrate	UV254 Absorbance
Unit	mg/L		°C	mg/L-N	mg/L-N	mg/L-N	mg/L-N	l/cm
Average	5.78	7.39	17.5	0.387	0.275	0.091	0.439	0.0958
5th Percentile	5.46	6.97	15.1	0.290	-	0.008	0.204	0.0895
95th Percentile	6.08	7.66	20.8	0.519	-	0.283	0.701	0.108

3.3.2 Ozonation Pilot System

The pilot ozone skid used for this project was designed and constructed by Intuitech™ (Salt Lake City, USA). The skid consisted of one countercurrent bubble diffusion column followed by four contact columns with several sample ports as depicted in Figure 4 below.

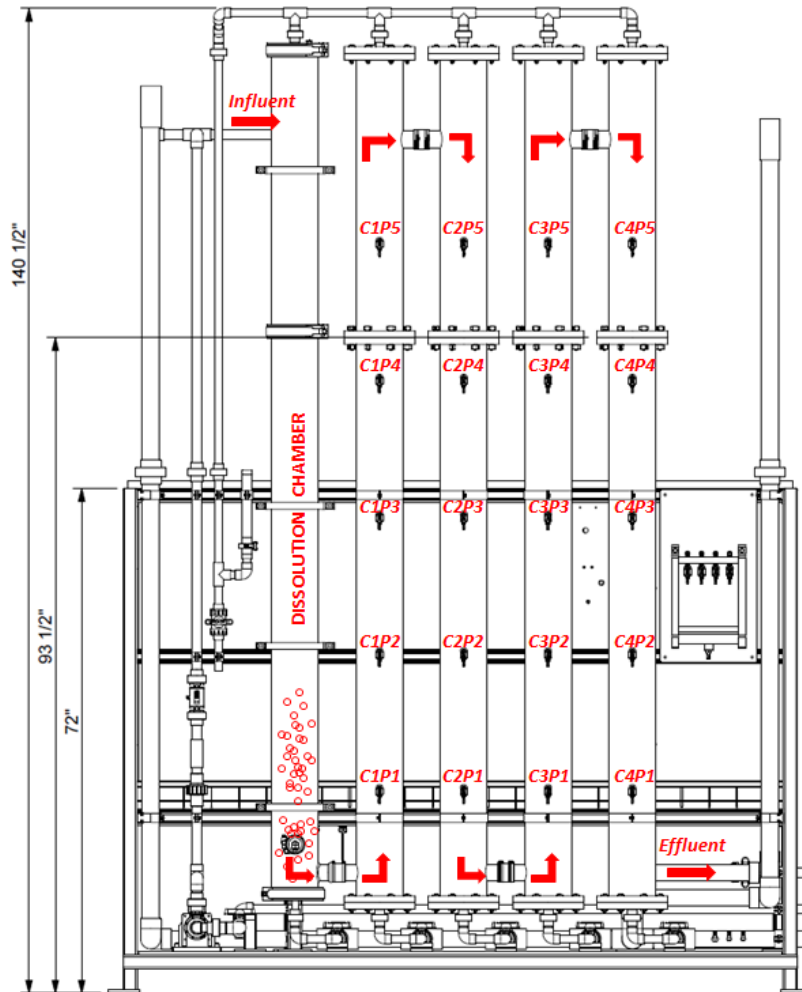


Figure 4- Ozone pilot skid

The system was operated continuously at 3.2 gpm (12.1 Lpm), the contact time of each column was approximately 4.2 minutes. Each of the contact columns had a series of sample ports to measure ozone residuals. Oxygen was concentrated from the air using the onboard oxygen concentrator and then fed into the ozone generator. Ozone dose was either set by a manual applied dose or controlled to a set dissolved residual concentration on one of the two ozone probes located in the contact columns.

3.3.4 Preformed Monochloramine System

Monochloramine was preformed prior to addition to the flocculation-sedimentation effluent (Figure 5). An iSpring RCC7 undersink reverse osmosis system was used to create carrier water to which sodium hypochlorite then ammonium sulfate were added using chemical metering pumps. The carrier water flow rate was set to achieve at least a 100x dilution of the chemicals to prevent heat buildup from monochloramine formation. A chlorine to ammonia ratio of 4.5 mg/L-Cl₂: mg/L-N was targeted for optimal monochloramine formation.

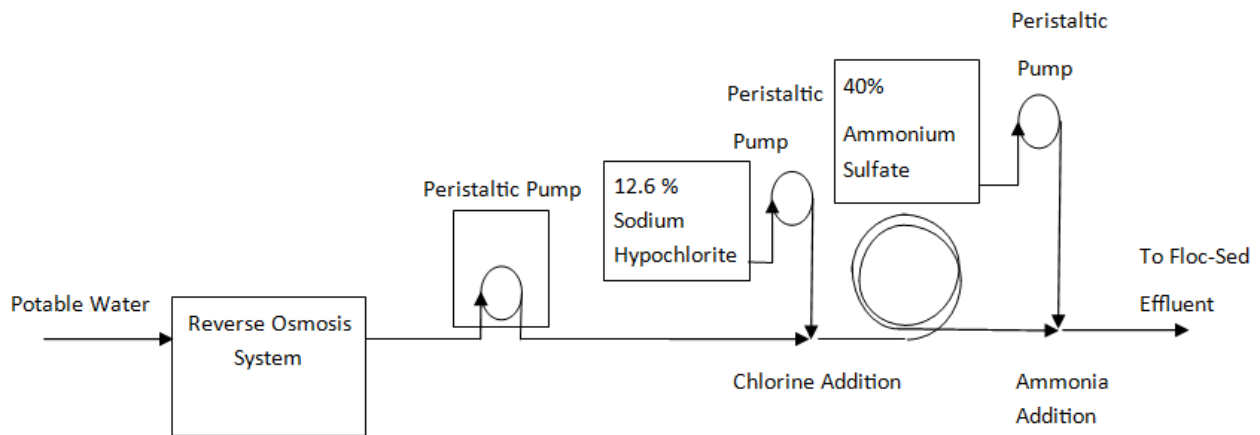


Figure 5- Pre-formed monochloramine system

3.3.5 Testing Plan

Ozone doses were selected to target O₃:TOC ratios of 0.5 to 2. Transferred ozone doses ranged from 3.3 to 10.8 mg/L and were adjusted for predicted nitrite demand to reach the desired O₃:TOC ratio. Monochloramine doses ranged from 0 to 5 mg/L-Cl₂. Due to the nature of the controls on both the ozone pilot and the monochloramine system, monochloramine dose was set, and then a series of ozone doses were tested. A single set of samples were collected after allowing the ozone dose to stabilize at the desired transferred ozone dose and then waiting one detention time (21 min) of the contactor. Monochloramine dose was then changed and the tests were repeated.

Table 2- Testing Matrices

One Day Test

Targeted O ₃ :TOC	0.5	1	1.5	2
NH ₂ Cl Dose (mg/L-Cl ₂)	0	3	5	

One Week Test

Targeted O ₃ :TOC	0.5	0.75	1	1.25	1.5	1.75
NH ₂ Cl Dose (mg/L-Cl ₂)	0	1	2	3	4	5

Both a one-day and one-week test matrix were conducted. For the one-day test four ozone doses were tested at three monochloramine doses over the course of a single day of operation to try to eliminate the effects of possible day to day changes in the influent. No ozone residuals were measured. During the one-week test, six ozone doses were tested at six monochloramine doses. Monochloramine dose was changed each day. Residual ozone concentrations were measured for each test.

3.3.6 Lab analysis

Bromate and bromide samples were preserved with ethylenediamine (EDA) and analyzed via ion chromatography (EPA Method 302). Ozone residuals were measured using the gravimetric indigo method (Standard Methods 4500-O₃). Malonic acid was added to mask any free chlorine and oxidized bromide species.

Table 3 summarizes the methods used for field testing. Online TOC measurements were used to calculate O₃:TOC ratios and monitor effluent TOC in the downstream biofilter (BAC Low in Figure 3). Monochloramine in the ozone pilot effluent was monitored to control sodium bisulfite feed to quench monochloramine prior to biofiltration.

Table 3- Lab testing methods

Parameter	Instrument	Method
pH & Temperature	Orion Star A211	
Total Chlorine	Hach SL1000 PPA	Hach USEPA DPD Chemkey Method 10260
Monochloramine	Hach SL1000 PPA	Hach Indophenol Chemkey Method 10270
Free Ammonia	Hach SL1000 PPA	Hach Indophenol Chemkey Method 10268
Total Ammonia (<1.5 mg/L-N)	Hach SL1000 PPA	Hach Indophenol Chemkey Method 10268
Total Ammonia (>1.5 mg/L-N)	Hach DR3900	TNT 831
Nitrite	Hach DR3900	TNT 839
UV254 Absorbance	Horiba Aqualog UV 800 C	
UV600 Absorbance (Indigo)	Horiba Aqualog UV 800 C	
Total Organic Carbon (TOC)	GE Analytical Instruments M5310C	
Online Monochloramine	Hach 5500SC	

3.4 RESULTS AND DISCUSSION

3.4.1 Bromate formation

For all ozone doses tested bromate was above the MCL without monochloramine addition. Bromate formation was reduced by as much as 97% with monochloramine addition at lower ozone doses but decreased at higher ozone doses. Data is summarized in Table 4.

Table 4- Bromate data from one week and one day tests

One-Week Test		Monochloramine Dose (mg/L-Cl₂)					
Targeted O ₃ :TOC	O ₃ Dose (mg/L)	0	1	2	3	4	5
		Bromate (µg/L)	Bromate (µg/L)	Bromate (µg/L)	Bromate (µg/L)	Bromate (µg/L)	Bromate (µg/L)
0.5	3.3	11.2	0.3	0.3	0.9	1.0	0.6
0.75	4.8	27.7	3.7	3.4	4.0	4.4	3.0
1	6.3	41.6	8.4	8.3	9.9	9.1	7.4
1.25	7.8	48.5	15.9	19.4	17.4	15.2	11.6
1.5	9.3	78.7	23.5	35.3	29.2	21.3	21.0
1.75	10.9	84.4	28.1	48.3	37.2	26.7	29.4
Bromide (µg/L)		437	410	390	417	431	

One-Day Test		Monochloramine Dose (mg/L-Cl₂)		
Targeted O ₃ :TOC	O ₃ Dose (mg/L)	0	3	5
		Bromate (µg/L)	Bromate (µg/L)	Bromate (µg/L)
0.5	3.3	10.1	1.42	0.32
1	6.3	37	10.2	4.23
1.5	9.1	78	24	12
2	12.5	109	44	26
Bromide (µg/L)		509	507	508

During the one week test there was no improvement in bromate suppression by increasing monochloramine from 1 mg/L-Cl₂ to 5 mg/L-Cl₂ for all ozone doses (Figure 6). Bromide samples were taken at the beginning of each day and concentrations ranged from 390 to 437 µg/L.

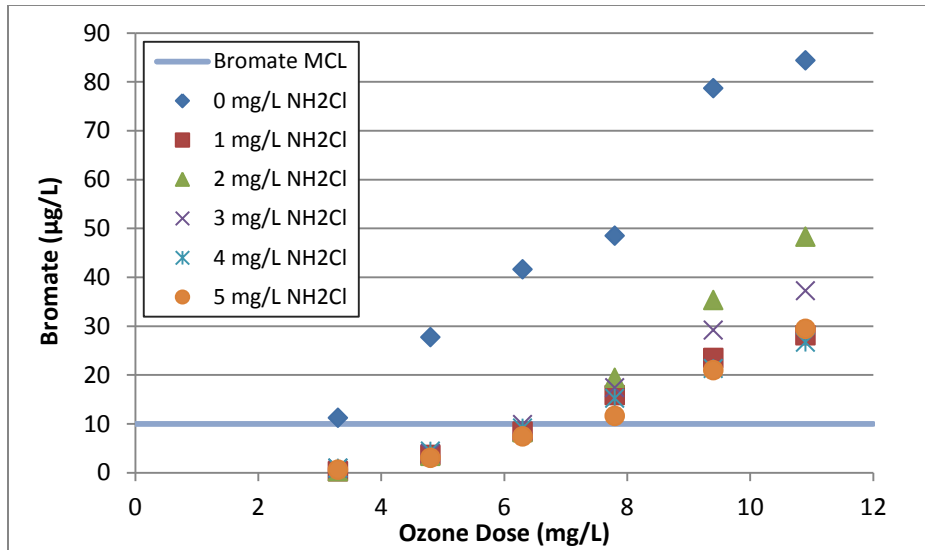


Figure 6- Bromate formation at varying O₃ and NH₂Cl doses

The two outlying points observed at 2 mg/L NH₂Cl are difficult to explain. The sampled bromide was 390 µg/L and the lowest of the week of testing. However, it may have spiked up later on in the day and caused these outliers as they did not correlate with an abnormal ozone exposure or change in UV absorbance (discussed in Sections 3.4.6 and 3.4.3 respectively).

During the one day test there was a distinct difference in bromate formation between the two NH₂Cl doses of 3 mg/L and 5 mg/L (Figure 7).

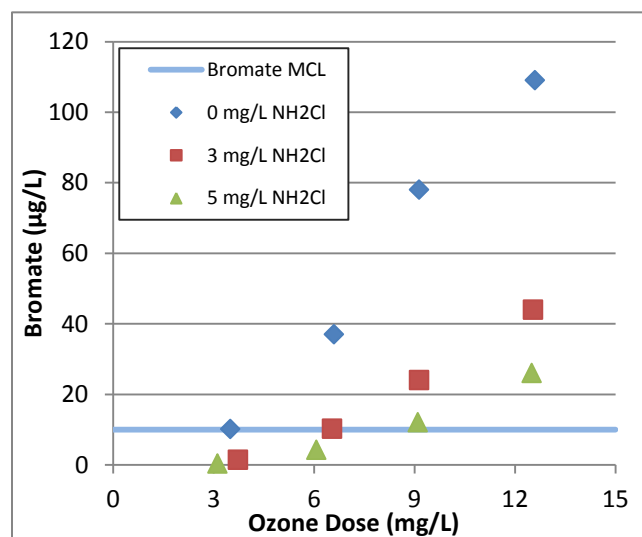


Figure 7- Bromate formation for one day test

At a realistic ozone dose of 1:1 O₃:TOC bromate was above the MCL at 10.2 µg/L with 3 mg/L NH₂Cl and safely below the MCL at 4.2 µg/L with 5 mg/L NH₂Cl. Bromide was 508 µg/L during the one day test. This could explain why there was a difference between the two monochloramine doses. Bromide spike testing showed a good correlation between bromide concentration and bromate formation and is presented in Appendix A.

Bromate formation increased linearly with ozone dose. The x-intercept was around 2.2 mg/L which is approximately the calculated instantaneous ozone demand (IOD) of the water which is discussed further in Section 3.4.4. This suggests that some measurable ozone exposure is required for bromate formation. The final step to form bromate from BrO₂⁻ requires ozone and this reaction is slower than those typically associated with initial phase reactions between ozone and DOM. *OH generation is limited when O₃:TOC < 0.25, possibly due to reactions with DOM including olefins and tertiary amines which do not propagate radical decomposition (Lee and von Gunten 2016).

Similar to both ammonia addition and the chlorine-ammonia process, monochloramine addition likely has a point where increasing dose has limited or no effect on controlling the bromate formation process (Buffle et al., 2004; Pinkernell & von Gunten, 2001). The location of this point is most likely water quality dependent. Benotti et al. (2011) saw no additional bromate suppression from increasing NH₂Cl from 1 mg/L to 2 mg/L while Ikehata et al. (2013) did. Interestingly Ikehata et al. had 35% lower bromide but higher pH and TOC which most likely increased their *OH generation and bromate formation for similar ozone doses. While some parameters fluctuated over the course of testing, mainly NO₂⁻, it is assumed that the nature and reactivity of DOM did not change.

3.4.2 Intermediate Masking

Free ammonia sufficient for bromamine formation, from both the wastewater plant effluent and excess from the preformed monochloramine system, was present for all tests. By comparing the rate constants for Equations 2 and 3 and the relative concentrations of free ammonia and

monochloramine, the amount of HOBr masked by NH₂Br and NHB_rCl can be calculated by a competition kinetics approach.

$$f_{HOBr \rightarrow NH_2Br} = \frac{C_{free\ NH_3} k_{NH_2Br}}{C_{free\ NH_3} k_{NH_2Br} + C_{NH_2Cl} k_{NHB_rCl}}$$

Where $f_{HOBr \rightarrow NH_2Br}$ is the fraction of HOBr that would form bromamine versus bromochloramine, $C_{free\ NH_3}$ and C_{NH_2Cl} are the concentrations of free ammonia and monochloramine in molar units respectively. k_{NH_2Br} and k_{NHB_rCl} are the second order rate constants for bromamine and bromochloramine formation through Equations 2 and 3 in units of M⁻¹s⁻¹.

For 5 mg/L-Cl₂ NH₂Cl and 0.32 mg/L-N free ammonia $f_{HOBr \rightarrow NH_2Br}$ was 0.989, this was the lowest calculated fraction of NH₂Br formation for all tests. In this case bromamine would form as the primary intermediate for HOBr rather than bromochloramine.

Due to the background ammonia, bromamines would also be formed in the control tests without NH₂Cl. The lowest observed ammonia concentration during control testing was 0.117 mg/L-N, this is sufficient to mask 0.667 mg/L Br as bromamine (79.9/14 = 5.71 mg/L Br per mg/L N). This suggests that radical scavenging is the primary benefit of monochloramine addition over ammonia addition alone when free ammonia is present. It should be noted that this may not be enough ammonia to re-mask HOBr as NH₂Br is oxidized to NO₃⁻ and Br⁻ becomes available for oxidation again.

3.4.3 Monochloramine as a Hydroxyl Radical Scavenger

Change in absorbance at 254 nm has been shown to be directly correlated with pCBA destruction and *OH exposure in the ozonation of multiple wastewater effluents (Wert et al., 2009b; Gerrity et al. 2012; Audenaert et al. 2013). Figures 8 and 9 show that, by this measure, monochloramine is acting as a hydroxyl radical scavenger.

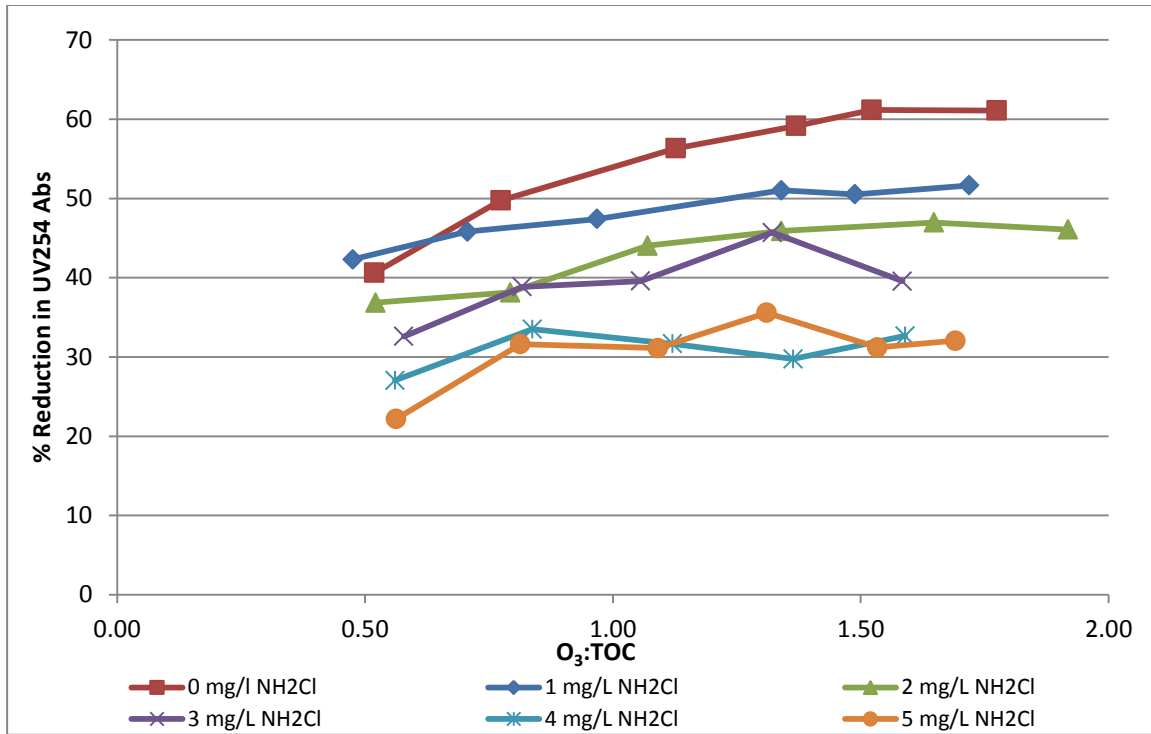


Figure 8- Change in UV absorbance at varying O₃ and NH₂Cl doses

Monochloramine showed no interference on initial UV absorbance measurements at 254 nm (illustrated in Appendix B). The trends for 0, 1, and 2 mg/L NH₂Cl show good correlations similar to those reported by Wert et al. (2009b) while the trends for 3-5 mg/L NH₂Cl are less certain. This could be due to the variability of pilot testing over a week of operation or testing error. Hydroxyl radical exposure continued to decrease with increasing monochloramine dose while bromate suppression remained the same.

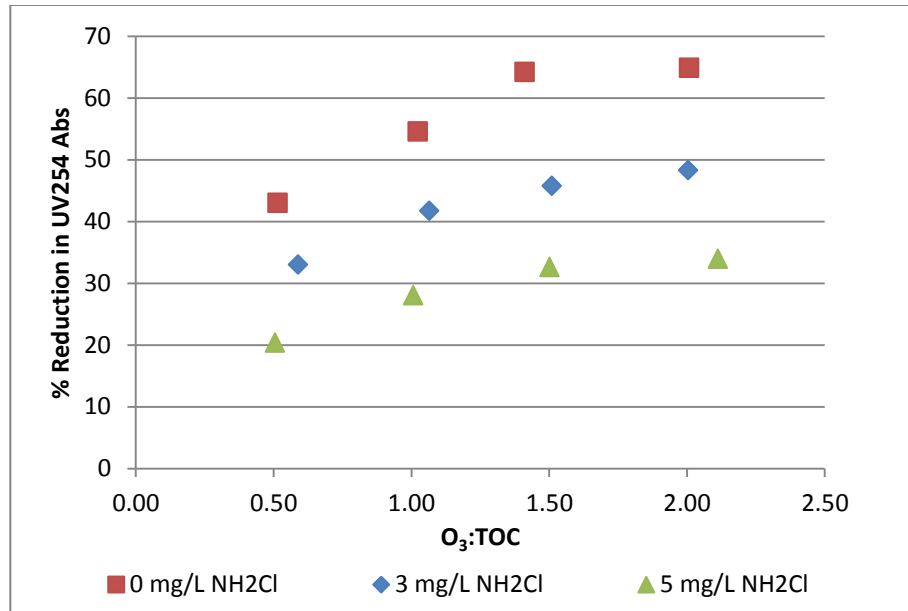


Figure 9- Change in UV absorbance at varying specific ozone dose for one day test

The relationships for the one day test in Figure 9 are much more consistent and defined. Gerrity et al. (2012) showed that change in UV254 absorbance was a good surrogate measure for hydroxyl radical exposure across multiple wastewaters and developed the following equation to estimate hydroxyl radical exposure:

$$\int[*OH]dt(Ms) = \frac{\ln(-0.0131 * [(1 - \frac{UV}{UV_0}) * 100\%] + 0.97)}{-5 * 10^9} \quad (6)$$

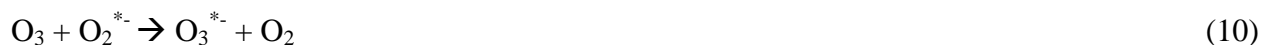
Applying this to the data in Figure 9 the approximate radical exposures can be found.

Table 5- Estimated *OH exposures and the effects on bromate formation

O ₃ :TOC	Estimated *OH exposure (Ms)			% Reduction in *OH Exposure		% Bromate Suppression	
	0 mg/L NH ₂ Cl	3 mg/L NH ₂ Cl	5 mg/L NH ₂ Cl	3 mg/L NH ₂ Cl	5 mg/L NH ₂ Cl	3 mg/L NH ₂ Cl	5 mg/L NH ₂ Cl
0.5	1.80E-10	1.24E-10	7.0E-11	31	61	86	97
1	2.73E-10	1.72E-10	1.0E-10	37	63	72	89
1.5	4.10E-10	1.99E-10	1.2E-10	52	70	69	85
2	4.25E-10	2.17E-10	1.3E-10	49	70	60	76

The estimated *OH exposures in Table 5, without the addition of monochloramine, are in line with those reported by Chys et al. (2017) and Lee and von Gunten (2016) on an O₃:TOC basis. The exposures with monochloramine may be lower than what actually occurred in the system.

The change in UV absorbance only represents the exposure seen by the organics and bromide, a portion of the *OH would react with NH_2Cl and would not be captured in change in UV absorbance. With monochloramine the decrease in radical exposure increased at higher ozone doses. At lower ozone doses direct reactions with DOM control hydroxyl radical generation (Equations 7 & 8).



At higher ozone doses once the most reactive DOM has been consumed, Equations 3 and 4 play a larger role in hydroxyl radical generation (Lee & von Gunten, 2016). Monochloramine would be able to reduce the *OH generated through this pathway and should decrease the ozone decay rate. Bromate suppression was not proportional to the reduction in hydroxyl radical exposure which indicates that radical scavenging is not the only mechanism of bromate suppression by monochloramine. At higher ozone doses more ozone is available to oxidize NH_2Br (and presumably $NHBrCl$) to nitrate and bromide. This bromide is then available to be re-oxidized to form bromate.

Reducing radical exposure by as much as 70 percent reduces bromate formation but it may also significantly limit the oxidation capacity of the system. Correlations developed by Gerrity et al. (2012) predict >80% removal of meprobamate, an antianxiety medicine commonly found in wastewater with low reactivity towards ozone ($k_{O_3} = 6 \text{ M}^{-1}\text{s}^{-1}$, $k_{^*OH} = 3(10^9) \text{ M}^{-1}\text{s}^{-1}$), at 50% reduction in UV 254 absorbance. Applying this to the data presented in Figure 9, it would take more than double the ozone dose to achieve the same degree of removal when adding 3 mg/L of monochloramine. However, in this case bromate would not have been below the MCL without monochloramine addition. If non-biodegradable, ozone recalcitrant compounds such as 1,4-dioxane and atrazine or meprobamate are an issue, use of monochloramine for bromate suppression may be problematic. On the other hand, many trace organic contaminants are oxidized quickly by ozone. Compounds such as Diclofenac or Sulfamethoxazole with $k_{O_3} > 10^4$

$M^{-1}s^{-1}$, are primarily removed by ozone despite their high reactivity with *OH . This is due to the relatively low concentrations of hydroxyl radicals. Using monochloramine for bromate suppression should come with serious evaluation of treatment objectives in wastewater and reuse applications.

3.4.4 Ozone Demand and Decay

The second phase of ozonation is traditionally modelled as first order decay in natural source waters. However, Buffle et al. (2006) showed that in wastewater ozonation the decay rate decreases with time following a power function. In this case, there are no distinct phases and the first order decay is actually a fixed rate. This behavior was not observable on the pilot scale. This could be due to testing inaccuracies and mixing in the contactor or being far enough into the power function that decay rate effectively is constant. For the sake of calculating decay rates and ozone exposure in the contactor, the decay rate is assumed to be constant in this study and was modeled as strict first order.

Decay rate was found using the first order regression of the dissolved ozone residual. IOD was then determined by back calculating the concentration of the outlet of the dissolution column and subtracting it from the transferred ozone dose. Decay rates decreased with increasing ozone dose (Figure 10). This is analogous to preozonation stabilizing the decay rate in subsequent ozonation steps (Buffle et al., 2006) where more ozone is available for reaction earlier. Initial or instantaneous ozone demand (IOD) was found by calculating the concentration at the outlet of the dissolution column using the first order regression of ozone decay and subtracting it from the transferred dose. IOD increased with increasing ozone dose but decreased as a fraction of the transferred dose (Figure 10). Even at the highest doses initial demand was greater than 50% of the transferred ozone dose.

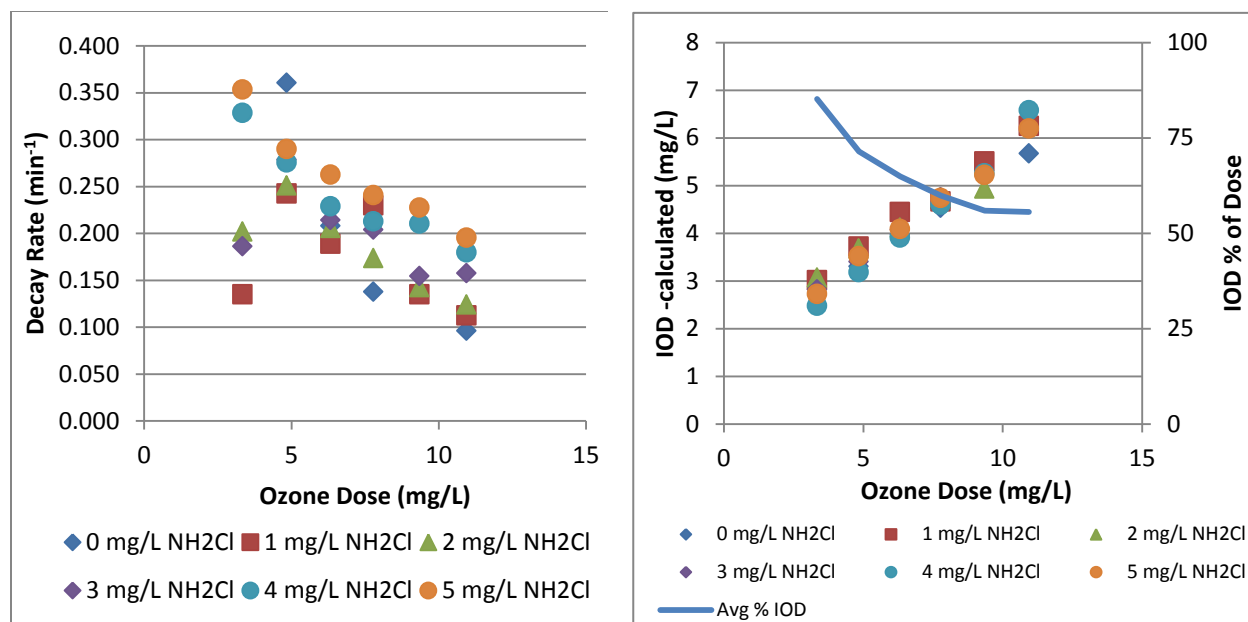
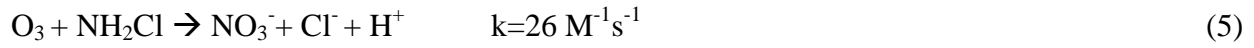


Figure 10- Effects of O₃ and NH₂Cl Dose on Ozone Decay Rate and IOD

Monochloramine addition did not stabilize the decay rate or decrease the initial demand of the water. As a radical terminator, monochloramine should prevent ozone decay through radical chain reaction (Equation 9). Initial phase ozone decomposition and ^{*}OH generation are primarily through direct reactions with DOM (Equations 7 & 8). As such the addition of a radical scavenger would not have any effect on initial decay or IOD. Benotti et al. (2011) showed a decrease in initial demand using monochloramine, however, monochloramine was formed in-situ by adding ammonia then HOCl rather than preforming in separate carrier water. Reactions between HOCl and certain DOM moieties containing primary and secondary amines are 10 to 100 times faster than the formation of NH₂Cl. This very small chlorine contact may decrease the IOD as these compounds would otherwise consume ozone and generate hydroxyl radicals (Buffle et al., 2004; Buffle & von Gunten, 2006; Deborde & von Gunten, 2008).

3.4.5 Nitrogen Mass Balance

In many cases it appeared that monochloramine increased the decay rate of ozone (Figure 10). Monochloramine is oxidized by ozone to form nitrate by Reaction 5 and could account for some increase in decay rate (W. R. Haag & Hoigné, 1984)



As shown in Figure 11, at higher ozone and monochloramine doses greater monochloramine oxidation was observed. Nitrite is quickly oxidized by ozone to form nitrate and exerts an ozone demand of 3.43 mg/L O₃ per mg/L-N NO₂⁻. Nitrite concentration ranged from 0 to 0.34 mg/L-N and was the changing water quality parameter with the most effect on ozonation. Free ammonia and nitrate varied throughout testing but do not react with ozone.

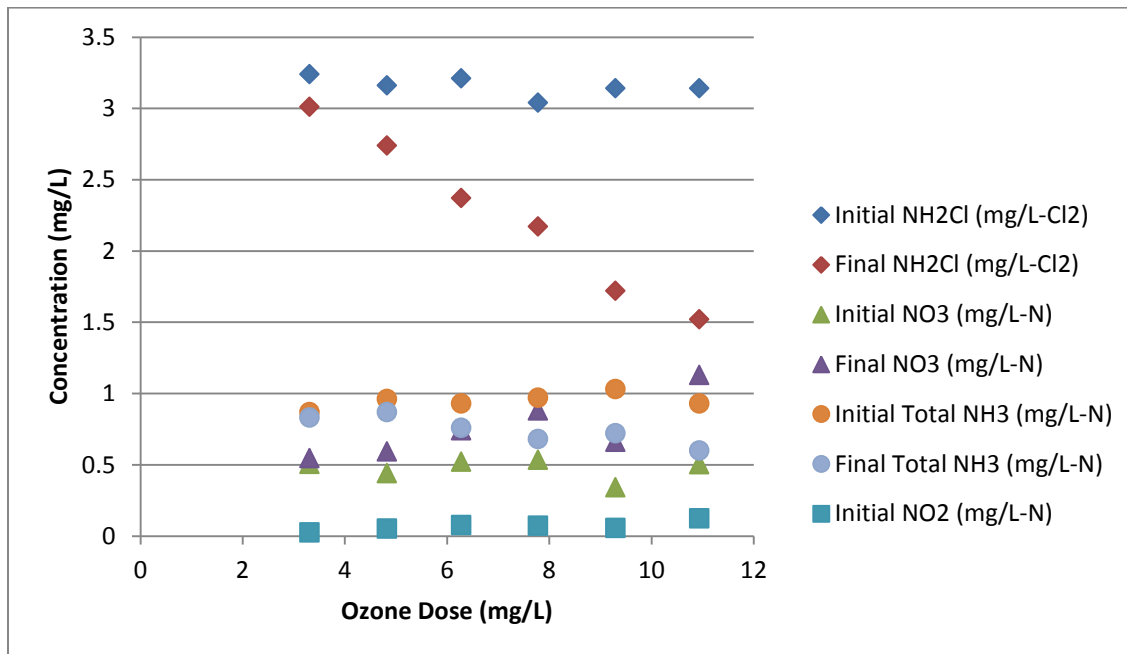


Figure 11- Nitrogen Species through Ozonation at 3 mg/L NH₂Cl

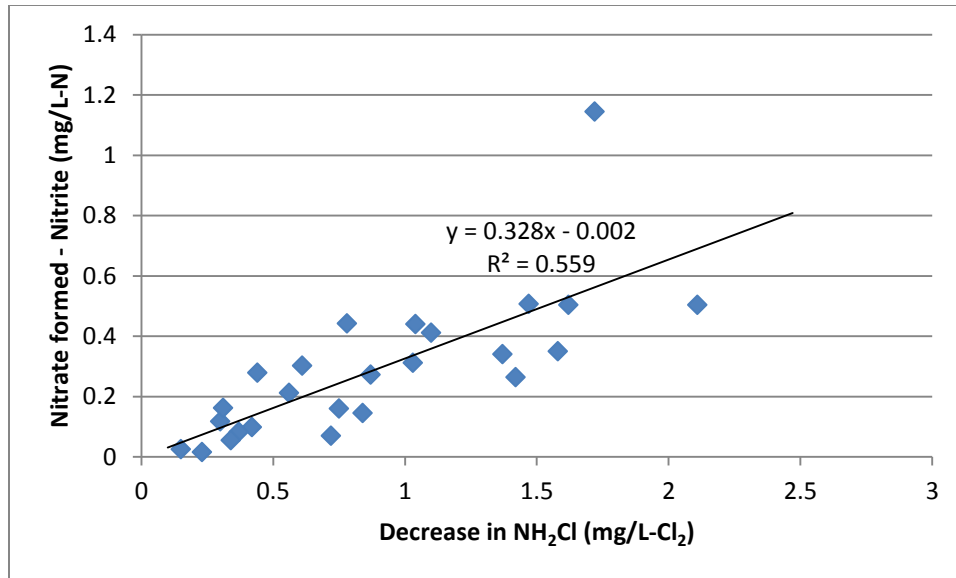


Figure 12- Monochloramine Destruction vs Nitrate Formation Corrected for Nitrite

Figure 12 shows a good correlation between monochloramine destruction and nitrate formation once corrected for nitrite oxidation. The ratio of 0.33 mg/L-N NO_3^- formed per 1 mg/L- Cl_2 NH_2Cl destroyed is greater than the stoichiometric amount of 0.20 mg N/mg Cl_2 via Equation 5. Bromamine, organic amines, and other dissolved organic nitrogen are also oxidized to form nitrate (de Vera et al., 2017; Lee & von Gunten, 2016).

3.4.6 Ozone Exposure

It is possible that increasing monochloramine also reduces bromate formation by reducing ozone exposure due to the increased ozone decay rate. Benotti et al. (2011) reported that it was necessary to increase the ozone dose by approximately 25% in order to achieve the same disinfection CT when adding monochloramine. In this case, ozonation conditions should be compared in terms of ozone exposure rather than purely on ozone dose.

Ozone exposures were calculated by integrating the first order residual profiles from the contactor. This does not account for the exposure that occurs in the dissolution column. Figure 13 shows that reduction in ozone exposure can be significant at higher ozone and monochloramine doses. In the normal operating range, around ~1:1 O_3 : TOC, the decrease was around 10% for 1 mg/L NH_2Cl and 20% for 5 mg/L NH_2Cl . The data obtained at lower ozone doses is more variable and does not correlate with monochloramine dose. Water quality

parameters including pH, temperature, TOC, and nitrite change throughout the day and may have a significant effect on ozone exposure.

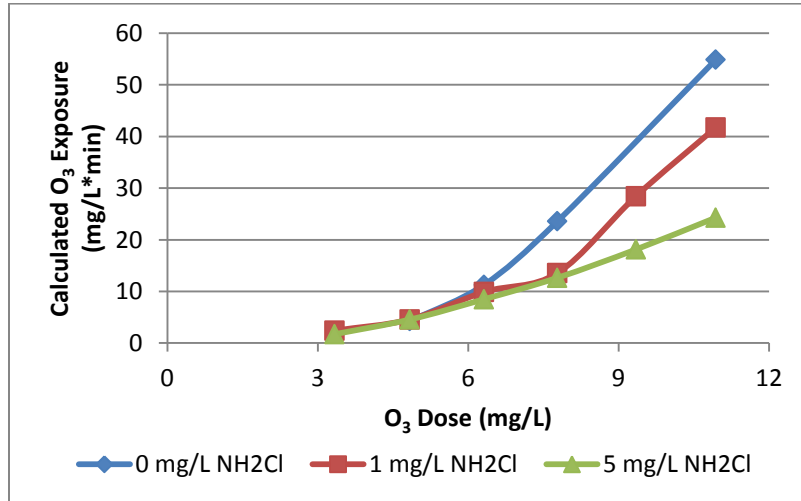


Figure 13- Effects of Monochloramine on Integrated Ozone Exposure

3.4.7 Disinfection Credit

Ozonation serves as one of multiple barriers against pathogens in HRSD’s SWIFT program. An internal project goal of 3-log virus inactivation credit was targeted. Disinfection CT was determined as the maximum of the measured ozone residuals times the corresponding detention time. Virus log removal values (LRV) were calculated by interpolation of the tables presented the EPA Disinfection Profiling and Benchmarking Guidance Manual (1999). The formulas used are in Appendix C, maximization of single point CT is discussed in Appendix D. Table 6 shows that the disinfection goal was easily met for all ozone doses where bromate was below the MCL.

Table 6- Selected Virus LRVs

NH ₂ Cl (mg/L-Cl ₂)	O ₃ :TOC		
	0.50	0.75	1.00
0		8.8	17.7
1	8.0	10.3	19.7
2	4.0	10.1	19.5
3	5.8	12.5	21.2
4	5.3	15.5	26.1
5	6.2	12.3	19.7

A baffle factor of 0.7 was used because no tracer testing had been conducted, this is likely very conservative as the columns used for the contactor should be closer to plug flow. Additionally, the single point CT method used is extremely conservative and greatly underestimates the ozone exposure in the contactor. At the higher ozone doses the calculated LRVs greatly exceeded the goal of 3-log virus inactivation credit. Ozone dose could be lowered further or the disinfection goals could be revised in order to target more disinfection credit.

Disinfection occurs primarily through molecular ozone (von Gunten, 2003a). As such, a radical scavenger such as monochloramine should have no negative impact on disinfection. However, because monochloramine increases decay rate and decreases ozone exposure it may be detrimental to disinfection performance. In this case, disinfection objectives may not have been met while below the MCL for bromate, making the negative of impacts of chloramination on oxidation and ozone exposure worthwhile.

3.4.8 Impact on Biofiltration

Over the course of testing TOC was monitored online on the ozone influent and the downstream biofilter effluent (BAC low in Figure 2). Increasing the ozone dose from 0.5 O₃:TOC to 2.0 O₃:TOC resulted in a 0.5 mg/L or 40% increase in TOC removal through the biofilters as shown in Figure 14. The tests were conducted over the course of one day and the changes were immediately apparent in the biofilter effluent.

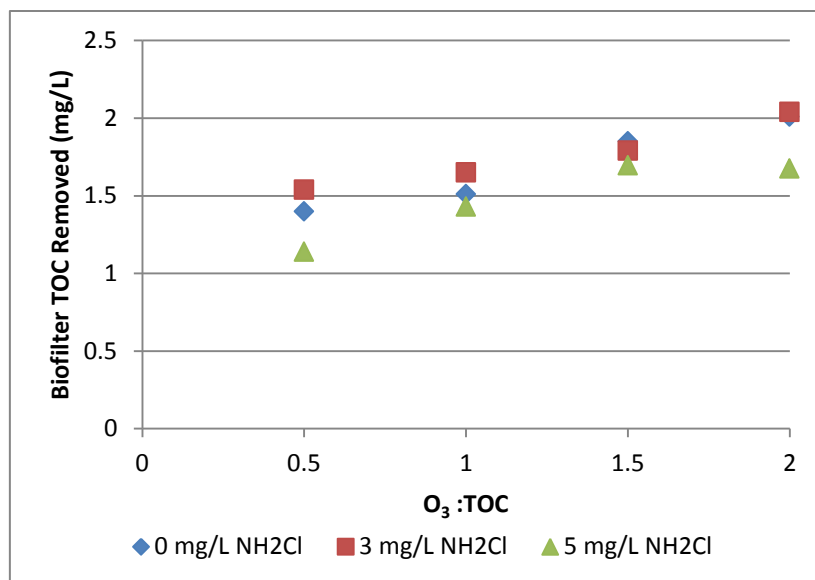


Figure 14- Effects of O₃ and NH₂Cl on TOC removed through the biofilter

AOC generation is influenced heavily by hydroxyl radical exposure (Wert, Rosario-Ortiz, et al., 2007). This could explain the slightly lower TOC removal at the higher monochloramine dose. However, this could also be explained by the decrease in ozone exposure due to monochloramine and is compounded by the lack of impact by 3 mg/L NH₂Cl. This is a fairly limited and uncontrolled data set. Further testing including lower ozone doses and long term operation should be conducted.

Increased monochloramine doses also would require higher chemical doses to quench the remaining chlorine prior to biofiltration. Additionally, until nitrification is established in the biofilters to remove the remaining ammonia, free chlorination downstream would be difficult.

3.5 CONCLUSIONS

This study set out to optimize ozone and monochloramine dose for bromate control in high bromide reuse water. Without monochloramine addition, bromate formation was above the MCL for all ozone doses tested so a chemical mitigation strategy was necessary. Monochloramine was able to control bromate formation to below the MCL at ozone doses up to 1:1 O₃:TOC. The

project disinfection objective of 3-log virus credit based on a single point CT was easily achieved even at the lowest ozone dose of 3.3 mg/L (0.5:1 O₃:TOC).

Bromate formation increased linearly with ozone dose after exceeding the IOD of the water. In some cases increasing monochloramine doses had no improvement on bromate suppression while in others it did. This is most likely water quality dependent and needs to be looked into further. In the case where increased monochloramine had no effect on further bromate suppression, ozone and hydroxyl radical exposure continued to decrease with increasing monochloramine dose. Overdosing monochloramine for a factor of safety may negatively affect treatment performance and operating cost without improving bromate control. Conversely, if monochloramine dose was chosen based on preliminary testing in which there was no additional bromate suppression with increasing dose, bromate may exceed the MCL due to changes in water quality.

Due to the free ammonia present sufficient for bromamine formation in all tests, the primary benefit of bromate suppression over ammonia alone is assumed to be radical scavenging by monochloramine. However, because this reduces the oxidation capacity of the system the use of monochloramine for bromate control requires careful evaluation of treatment objectives. Monochloramine had no effect on initial demand, which is expected as a hydroxyl radical scavenger would have little effect on ozone consumption in the initial phase. Therefore the decrease in demand seen by others may be due to reactions of chlorine with DOM when forming monochloramine in-situ. Despite being a hydroxyl radical scavenger, monochloramine increased ozone decay rate. This could be due to ozone oxidizing monochloramine to form nitrate, however further study in a more controlled setting is required.

Increasing ozone dose from 0.5 to 2.0 O₃:TOC lead to a 0.5 mg/L increase in TOC removed through the downstream biofilter. This may justify increasing ozone dose beyond where disinfection objectives are met. However, in the range where bromate was controlled, 0.5 to 1 O₃:TOC, the increase was only around 0.1 mg/L.

4 Manuscript 2- Ozone exposure and dissolution system considerations for Bromate formation and control in high bromide reuse waters.

4.1 Abstract

Detailed pilot testing was conducted in order to better understand the implications of ozone dissolution systems on bromate formation and control in a reuse scenario. Testing showed that the majority of bromate was formed in the bubble diffusion column, likely due to increased hydroxyl radical exposures. Preformed monochloramine was used to suppress bromate and reduced both final bromate formation and bromate formed in the dissolution zone. This differs from other chemical bromate mitigation strategies which do not control bromate formation through the indirect *OH pathways and implies that monochloramine is acting as a radical scavenger. In sidestream injection systems as much as 14 $\mu\text{g/L}$ of bromate was formed in a 23.5 second the sidestream before blending. However, this can be reduced by monochloramine addition and decreasing detention time. Efforts should be made in both design and operation to minimize uncredited ozone exposure and bromate formation in the dissolution zone.

4.2 INTRODUCTION AND BACKGROUND

Ozonation has been practiced in water and wastewater treatment for many years in order to provide oxidation and disinfection while limiting disinfection byproduct formation associated with chlorination. More recently ozonation combined with biologically active carbon filtration (BAC) has gained attention in wastewater and reuse applications for its advanced oxidation capacity and as a barrier against pathogens (Gerrity et al., 2011, 2014).

Ozone acts as a twofold oxidant through both molecular ozone (O_3) and decomposition into hydroxyl radicals (*OH). Ozone decomposition occurs due to direct reactions with dissolved organic matter (DOM) and autocatalytically. Ozone decay follows multiphasic kinetics; the initial rapid “instantaneous” decay which produce high *OH concentrations in the first 20 to 30 seconds is controlled by ozone reacting directly with DOM. This is followed by a more stable second phase in which ozone decay follows a first order pattern. Due to the higher concentration

and reactivity of DOM in wastewater effluent, ozonation acts as an advanced oxidation process (Buffle et al., 2006).

Bromate is a possible carcinogen formed through the ozonation of bromide. Bromate forms through a complex series of reactions with ozone and hydroxyl radicals. In the direct pathway bromide is oxidized to bromate through reactions with ozone. The direct-indirect and indirect-direct pathways consist of reactions with both ozone and hydroxyl radicals (Pinkernell & von Gunten, 2001). Bromide may be present in higher concentrations in wastewater reuse applications due to industrial sources or saltwater infiltration. Because of these higher concentrations, larger ozone doses, and higher $^{\bullet}\text{OH}$ yields, controlling bromate formation to below the maximum contaminant level (MCL) of 10 $\mu\text{g/L}$ becomes vital in potable reuse applications. Monochloramine (NH_2Cl) addition has been shown to effectively control bromate formation by acting as a hydroxyl radical scavenger and masking bromide from further oxidation as either NH_2Br or NHBrCl (Benotti et al., 2011; Buffle et al., 2004; Gazda & Margerum, 1994; Ikehata et al., 2013).

Ozone gas must be generated on site and then transferred into the water for treatment. Mass transfer has traditionally been achieved by bubble diffusion. However, with the introduction of medium frequency ozone generators, which produce ozone at up to 12% by weight, sidestream injection has recently gained prevalence. In sidestream systems a portion of the flow is pulled off and high concentrations of ozone are added by a venturi injector before being mixed back in with the bulk flow. These systems eliminate the need for deep contactors to maximize pressure for transfer efficiency and confined space entry concerns for regular diffuser maintenance. Sidestream injection systems are often more expensive due to the pumping costs but are more operator friendly. However, these systems may allow disinfection goals to be met at a lower ozone dose (Wert et al., 2016).

Ozone and hydroxyl radical exposures represent their respective concentrations integrated over time. They are important parameters for estimating the oxidation of both contaminants and bromide for bromate formation. For a given water quality, hydroxyl radical exposures are the same at the same ozone exposure, regardless of ozone dose (Buffle et al., 2006). Because of this,

bromate formation is often reported in terms of ozone exposure rather than time which allow results to be compared between ozone doses and different waters. Traditional methods for measuring ozone exposure in pilot and full scale contactors, such as the extended integrated CT_{10} method, do not account for ozone exposure occurring in the dissolution zone which can lead to serious underestimation of contaminant oxidation and byproduct formation (Rakness et al., 2005; Wert et al., 2009a).

Disinfection credit is awarded based CT which serves as a conservative estimate of ozone exposure. CT is calculated based on the residual ozone concentration times the detention time at one or several residual sample ports. CT is only measured in the disinfection or compliance zone of the contactor which occurs downstream of mass transfer in both fine bubble diffusion and sidestream injection systems.

Measuring ozone exposure occurring in the instantaneous or initial ozone demand (IOD) phase on the pilot scale has traditionally been difficult. Wert et al. (2016, 2017), showed that ozone exposures up to 2.85 mg/L-min and as much as 9.1 $\mu\text{g/L}$ bromate formed in the diffusion column of a drinking water treatment pilot where no disinfection credit is given. High bromate concentrations were also formed in the sidestream; however, this could be minimized if detention time is limited.

Hampton Roads Sanitation District's Sustainable Water Initiative for Tomorrow (SWIFT) is an indirect potable reuse project which aims to treat wastewater treatment effluent to drinking water standards before injecting into the Potomac Aquifer. Ozone-BAC is central to this treatment process. Pilot testing of the treatment train began in June 2016 while the one million gallon per day (MGD) SWIFT Research Center began operation and aquifer augmentation in May of 2018. Full scale implementation is planned to be completed at five treatment plants by 2030 totaling approximately 100 MGD. However, due to salt water infiltration and industrial sources, high bromide concentrations, from 130 $\mu\text{g/L}$ to greater than 1000 $\mu\text{g/L}$, are present at all the treatment plants. Mitigating bromate formation is a chief concern in the implementation of this process. Understanding the impact of contactor design and setup on bromate formation is critical to the design of future systems.

The aim of this study was to quantify ozone exposure and bromate formation occurring in the dissolution zone in light of total ozone exposure and the final effluent bromate concentration. The addition of monochloramine as a chemical bromate mitigation strategy and its effects on bromate formation was also analyzed in the dissolution zone. Additionally, direct comparison between fine bubble diffusion and sidestream injection with varying detention times was attempted in order to understand the implications of dissolution systems in reuse scenarios with high bromide concentrations and simulate the sidestream at the SWIFT Research Center. A range of ozone doses from 2 to 7 mg/L (~0.25-1 O₃:TOC) and monochloramine doses from 0 to 5 mg/L-Cl₂ were tested to understand how a variety of conditions effected ozone exposure and bromate formation.

4.3 MATERIALS AND METHODS

4.3.1 Pilot Treatment Plant

In order to demonstrate the treatment capabilities of the SWIFT treatment process, a pilot treatment plant was operated at HRSD's York River Treatment Plant. The pilot consisted of coagulation, flocculation and sedimentation, ozonation, biologically active carbon filtration and granular activated carbon adsorption followed by UV disinfection. York River Treatment Plant uses primary clarification with ferric addition followed by fully nitrifying conventional activated sludge and tertiary denitrification filters and chlorine disinfection. The pilot was fed filter effluent prior to final disinfection. Mixed liquor was added to the pilot feed to increase total suspended solids to approximately 5 mg/L to simulate other treatment plants without tertiary filtration. A chiller unit was installed at the head of the pilot to lower the temperature to 15°C to simulate winter conditions.

The flocculation sedimentation skid was designed and constructed by Intuitech (Salt Lake City UT) and consisted of two stage rapid mix followed by three stage tapered flocculation and a lamella plate clarifier. Aluminum chlorohydrate (ACH) was fed in the first rapid mix stage and cationic polymer was fed in the second.

4.3.2 Ozonation Pilot

The ozone pilot skid was also manufactured by Intuitech. The ozonation system operated at 3.2 gpm and consisted of one 4.2 minute counter current dissolution column with a bubble diffuser at the bottom. Four downstream contact columns with five sample ports each followed the dissolution column. Ozone was generated from oxygen from the onboard oxygen concentrator. Ozone dose was controlled by setting the desired applied dose. Transfer efficiency was calculated based on the concentration measured by the off gas analyzer that pulled off the top of the dissolution column.

To measure ozone residuals, ozone exposure, and take bromate samples from the dissolution column, a new column with 12 sample ports was constructed (Figure 15). The top nine sample ports were spaced every 22.4 seconds down the column starting 29 seconds after water entered the top of the column. Ports 10-12 were located approximately 12 seconds apart. The lowest was 9 seconds above the diffuser.

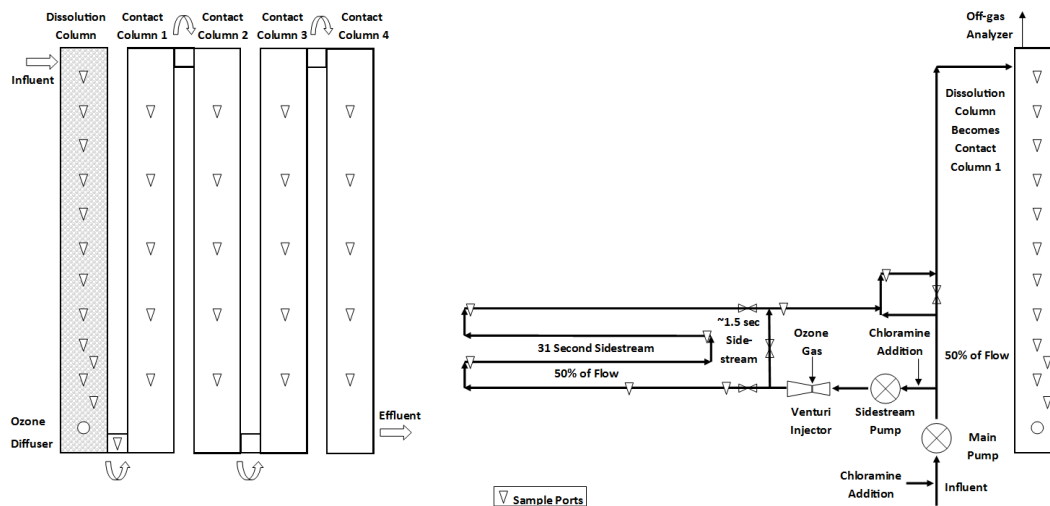


Figure 15- Ozonation pilot configuration with dissolution column for sampling (left) and sidestream injection (right)

In order to compare between fine bubble diffusion and sidestream injection, as well as attempt to simulate the ozonation system at the SWIFT Research Center, a sidestream with venturi injector was added (Figure 15). In this configuration 50% of the flow (1.6 gpm) was pulled off using a

second pump and ozone was added using a venturi injector (Mazzei, Bakersfield CA). The ozonated flow could either pass through a 31 second or a 1.5 second sidestream before mixing back with the non ozonated water followed by a static mixer. The mixed flow then entered the top of the dissolution column which acted as a contact column in the sidestream configuration. Ozone transfer efficiency was based off the measurement by the off gas analyzer on the top of the first column. Five sample ports were installed along the sidestream in order to measure bromate and ozone residuals. For the bromate testing in section 4.4.6 the sidestream flow rate was increased to 2.1 gpm in order to achieve suction on the venturi at higher gas flow rates required for higher ozone doses, this reduced the detention time to 23.5 seconds.

4.3.3 Preformed Monochloramine

Monochloramine was preformed in a separate carrier water prior to addition to the flocculation-sedimentation effluent. Sodium hypochlorite then ammonium sulfate were added to reverse osmosis water from an iSpring RCC7 under sink treatment system. A 100x dilution was targeted to reduce heat buildup from NH_2Cl formation. Chemical addition was controlled using chemical metering pumps in order to target a 4.5:1 Cl_2 :N ratio for optimal formation of only monochloramine.

4.3.4 Analytical methods

Bromide and bromate samples were collected simultaneously and preserved with ethylenediamine (EDA) before being analyzed by ion chromatography (EPA Methods 300 & 302 respectively). Ozone residuals were measured via the gravimetric indigo method with the addition of malonic acid to minimize interferences by any free chlorine or oxidized bromide species (Standard Methods 4500- O_3). Testing methods are summarized in Table 7. For monochloramine samples taken in the presence of ozone, NaNO_2 was dosed in excess in order to quench any remaining ozone. Nitrite is quickly oxidized to nitrate by ozone and neither interferes on the DPD method used for chloramine (Benotti et al., 2011).

Table 7- Lab testing methods

Parameter	Instrument	Method
pH & Temperature	Orion Star A211	
Total Chlorine	Hach SL1000 PPA	Hach USEPA DPD Chemkey Method 10260
Monochloramine	Hach SL1000 PPA	Hach Indophenol Chemkey Method 10270
Free Ammonia	Hach SL1000 PPA	Hach Indophenol Chemkey Method 10268
Total Ammonia (<1.5 mg/L-N)	Hach SL1000 PPA	Hach Indophenol Chemkey Method 10268
Total Ammonia (>1.5 mg/L-N)	Hach DR3900	TNT 831
Nitrite	Hach DR3900	TNT 839
UV600 Absorbance (Indigo)	Horiba Aqualog UV 800C	
Total Organic Carbon (TOC)	GE Analytical Instruments M5310C	
Online Monochloramine	Hach 5500SC	

4.3.5 Calculations

Ozone exposure in the dissolution column was calculated by summing the trapezoidal areas based on ozone residual and time between the points.

$$\text{Column Ozone Exposure: } O_3 \text{exp}_{\text{column}} = O_3 \text{exp}_{n-1} + C_{O_3-1}(t_2 - t_1) + 1/2 * (C_{O_3-2} - C_{O_3-1})(t_2 - t_1)$$

where $O_3 \text{exp}_{n-1}$ is the ozone exposure at the previous port. It was assumed that the ozone concentration at inlet of the column was zero.

Cumulative ozone exposure in the contactor was calculated by integrating the first order regression equation to the desired time and adding it to the ozone exposure from the dissolution column.

$$1^{\text{st}} \text{ order decay: } C = C_0 e^{-kt}$$

$$\text{Contactor Ozone Exposure at any time, t: } O_3 \text{Exposure} = O_3 \text{exp}_{\text{column}} + (1 - e^{-kt}) \frac{C_0}{k}$$

Instantaneous or initial ozone demand, IOD was calculated as the difference between the transferred ozone dose and the residual concentration at the outlet of the dissolution column.

4.4 RESULTS AND DISCUSSION

4.4.1 Bubble Diffusion Column

Ozone residuals were collected down the pilot dissolution column in order to quantify ozone exposure. Figure 16a shows a typical dissolved ozone concentration profile.

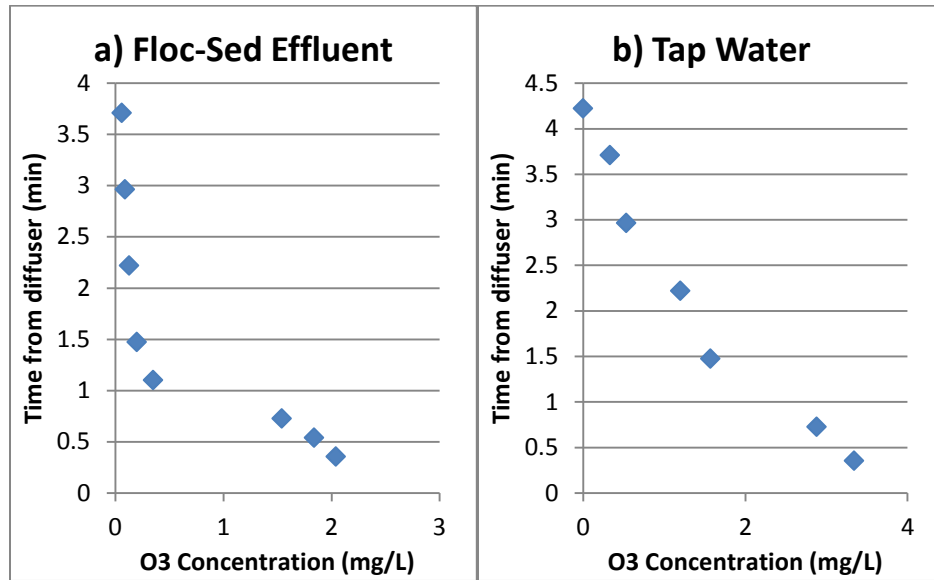


Figure 16- Dissolved ozone concentration down the dissolution column for 5.3 mg/L transferred ozone dose in a) floc-sed effluent and b) tap water

A measurable residual was established toward the bottom of the dissolution column. In a counter-current orientation, small amounts of ozone are transferred to the water at the top of the column which react extremely quickly with dissolved organic matter in the water. As the water flows down, ozone continues to be transferred and be consumed until the demand of the fastest reacting species is met. Quantifying the decay and demand in the dissolution column is difficult; ozone residual continues to increase with depth and ozone demand increases with ozone dose (Buffle et al., 2006; Rakness, 2005). Potable water was run through the pilot at the same ozone dose and is shown in Figure 16b. When compared to Figure 16a, the difference in both shape and maximum residual demonstrates this ozone demand. The tap water has a lower TOC and was preozonated in the drinking water treatment process. However, there is still some demand as the maximum O_3 residual does not appear to approach the transferred ozone dose of 5.3 mg/L.

When ozone is applied at one time, decay is typically considered to follow biphasic kinetics consisting of a rapid initial phase in roughly the first 20 seconds followed by a slower second phase which follows pseudo first order decay (von Gunten, 2003a). Initial phase ozone reactions with DOM in wastewater effluent are extremely fast and result in rapid ozone consumption (Buffle et al., 2006). Due to the 4.2 minute detention time in the pilot column, some combination of initial and second phase kinetics is occurring.

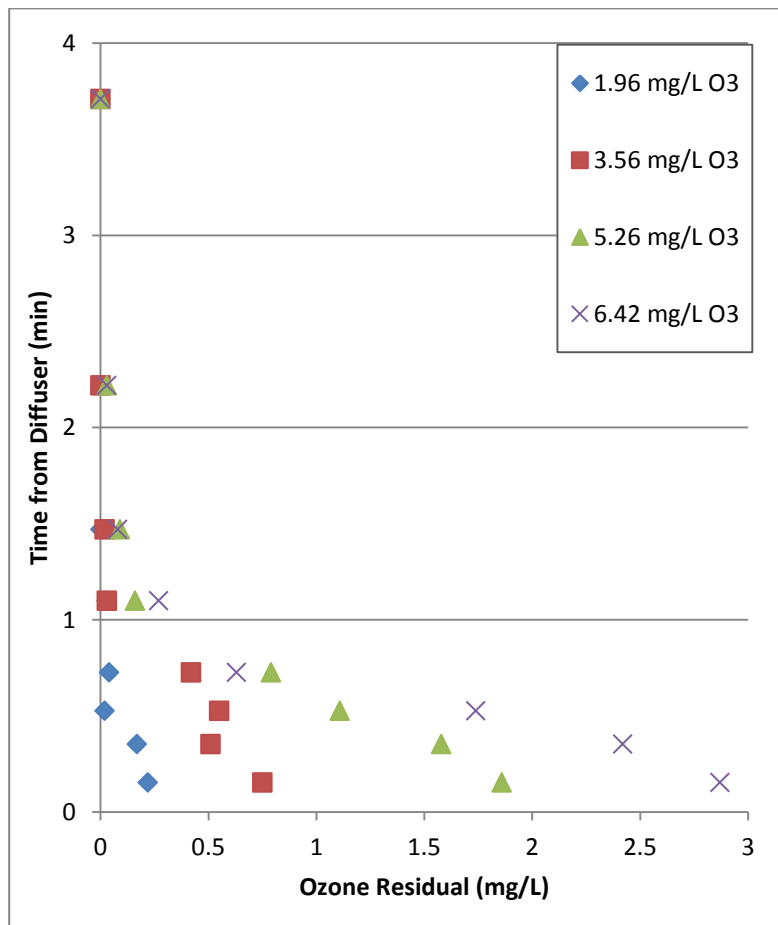


Figure 17- Dissolved ozone concentration in the dissolution column

Figure 17 shows the residual ozone profile for multiple ozone doses. Residual was established further up the column with increasing dose but was still mostly toward the bottom compared to the more triangular profile of the tap water. This further illustrates the variability of ozone demand as the measured residual closest to the diffuser is not a set amount less than the transferred ozone dose.

It should be noted that the 4.2 minute detention time of the pilot dissolution column is longer than the typical 1-3 minutes found in most water treatment plants and represent turndown flow conditions. If a shorter detention time were used the residual would be established even further down the column (Wert et al., 2016). The IOD, ozone exposures, and corresponding bromate formation presented here are likely higher than what would be seen in typical plant operation at design flow.

4.4.2 Dissolution Ozone Exposure and Bromate Formation

Ozone exposure in the dissolution column was calculated by finding trapezoidal area between residual points in terms of time and concentration. Bromate samples were also collected along the dissolution column.

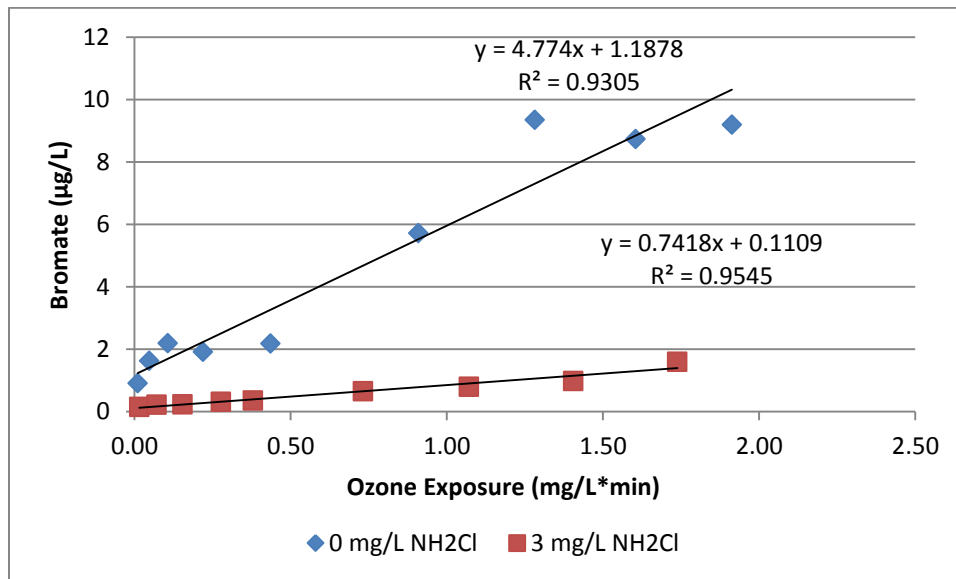


Figure 18- Bromate formation in the dissolution column

Bromate increased linearly with ozone exposure in the dissolution column (Figure 18). A similar result was seen by Wert et al. (2016). This shows the effects of ozone being applied over time; typical bench testing results show rapid bromate formation at low ozone exposures followed by a slower formation rate further on (Buffle et al., 2004; Pinkernell & von Gunten, 2001). This is due to the higher hydroxyl radical concentrations generated during the initial phase. To the author's

knowledge, no bromate testing has been conducted within the initial phase of ozonation using a quench flow system or similar.

Monochloramine addition significantly reduced bromate formation in the dissolution column at comparable ozone exposures. This is consistent with the hypothesis that monochloramine is acting as a hydroxyl radical scavenger. During the initial phase direct reactions with DOM cause large hydroxyl radical yields. The addition of a scavenger would not prevent the formation of $^{\bullet}\text{OH}$ through these reactions. However, with monochloramine present fewer hydroxyl radicals will be able to react with bromide. This differs from other typical bromate control strategies which do not usually have any effect on bromate formation in the initial phase. Ammonia addition only prevents bromate formation through the direct ozone pathway by masking HOBr as NH_2Br . Monochloramine may also be masking HOBr as NH_2Br or NHBrCl . pH depression controls ozone decomposition in the second phase of ozonation, however, radical generation in the initial phase is through direct ozone reactions with DOM and is not strongly influenced by pH (Buffle & von Gunten, 2006; Pinkernell & von Gunten, 2001). Pilot testing by Wert, Neeman et al. (2007) found that the chlorine-ammonia process did not have much impact on bromate formation in the dissolution chamber.

4.4.3 Total Ozone Exposure and contactor Bromate formation

Figure 19 shows dissolved ozone concentration, ozone exposure, and bromate formation throughout the ozonation system. In this case, 26% of the total ozone exposure occurred in the dissolution column while 55% of the final bromate was formed. This shows the importance of the initial phase hydroxyl radical reactions that occur in the dissolution column. The ozone residual decay profile was perfectly first order in the downstream contact columns so it is assumed that all initial phase reactions take place in the dissolution column. Extending the trendline back in time nearly perfectly matches the ozone residual at the diffuser.

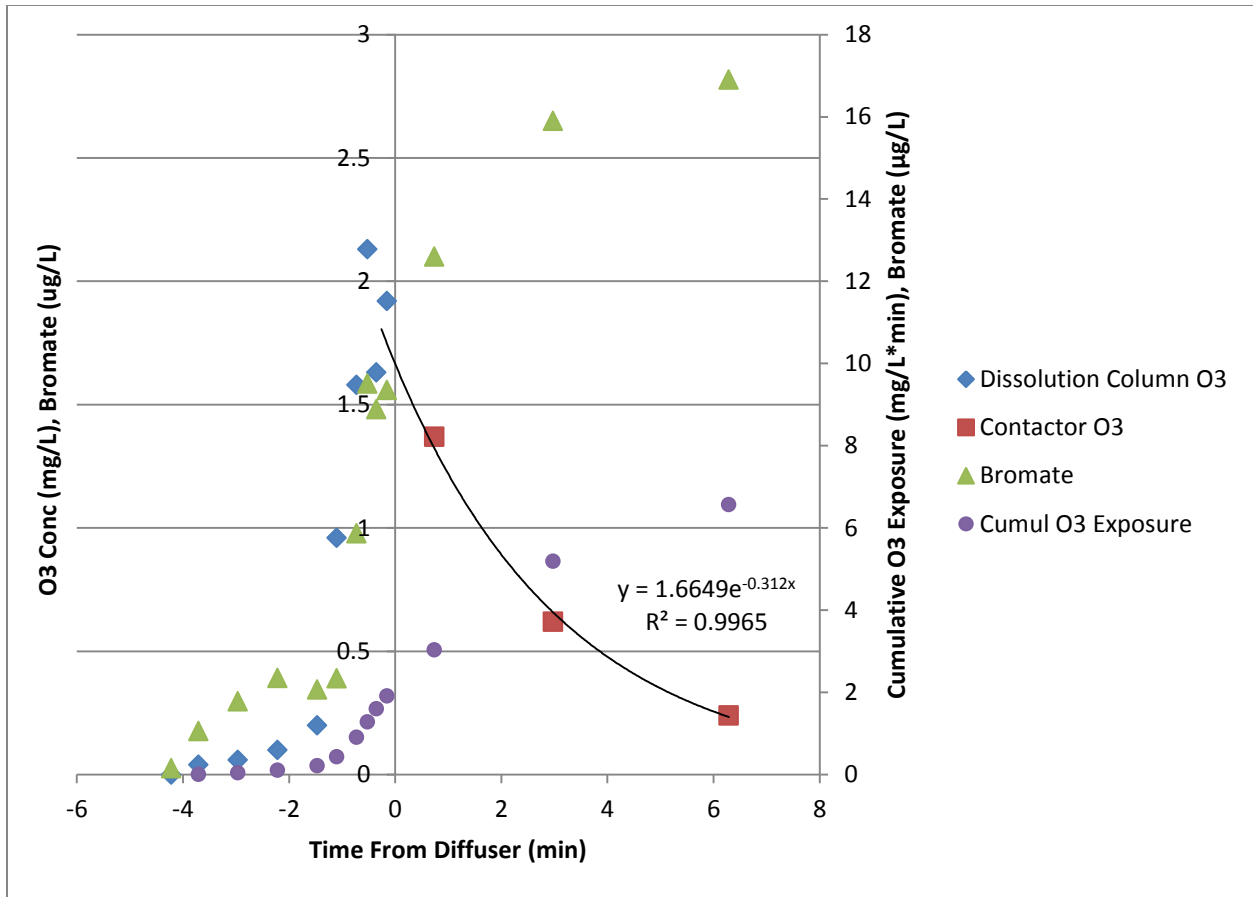


Figure 19- Ozone concentration, exposure, and bromate formation profile for no NH₂Cl, 5.5 mg/L O₃ Dose

A nearly identical residual profile was collected immediately after the one presented above but with the addition of 3 mg/L-Cl₂ monochloramine and is shown in Figure 20. Previous testing had indicated that monochloramine increases decay rate and decreases ozone exposure, however, only a slight change in decay rate was seen here that may be due to other variations in the water quality.

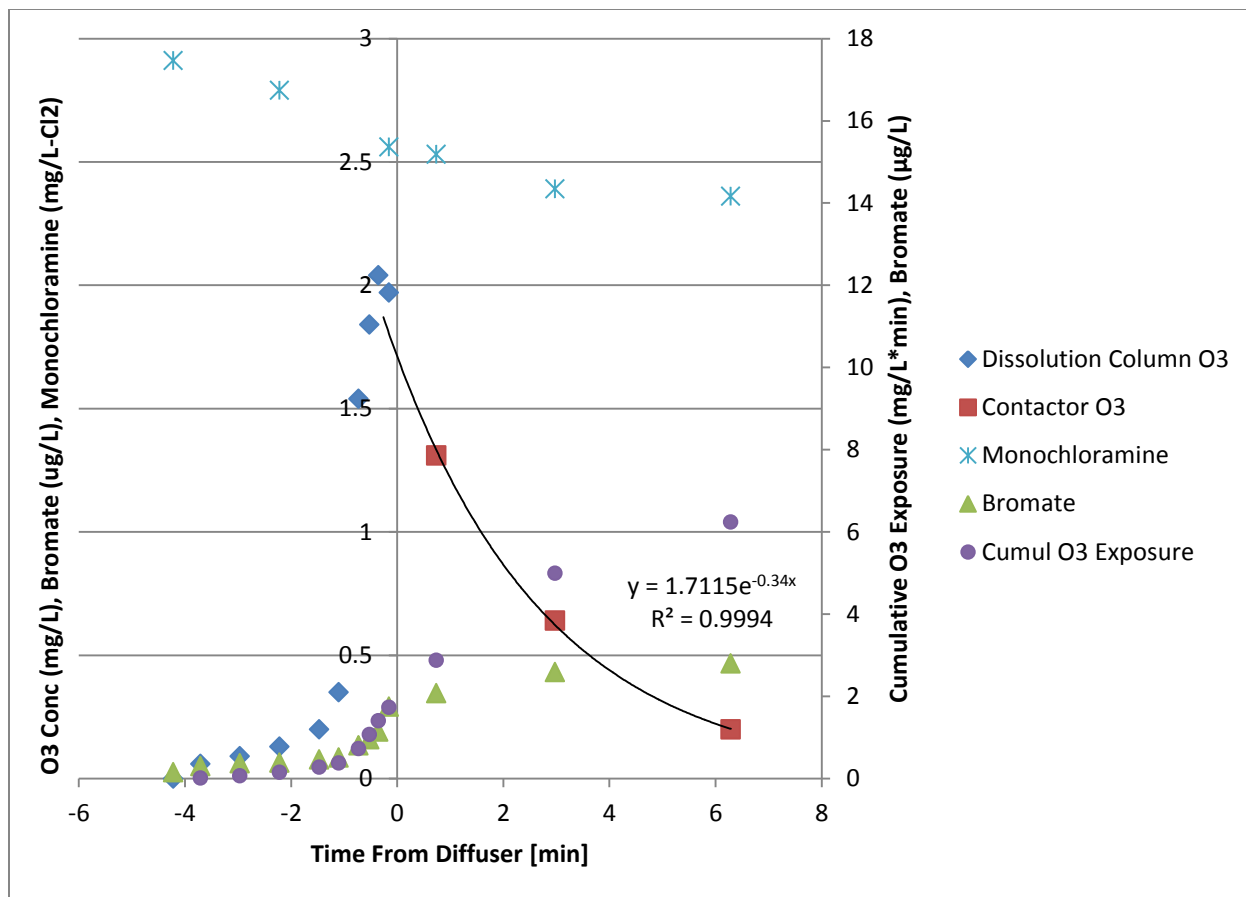


Figure 20- Ozone concentration, exposure and bromate profile for 3 mg/L NH₂Cl, 5.5 mg/L O₃ Dose

With monochloramine, final bromate formation decreased by 84% from 16.7 to 2.7 µg/L. Similar to the test without chloramine, 25% of total ozone exposure occurred in the dissolution column while 60% of bromate was formed. Monochloramine was slowly oxidized throughout the contactor. When compared to cumulative ozone exposure (Figure 21), bromate increased quickly and nearly linearly in the dissolution column. Bromate formation then slows down and levels off in the contactor as hydroxyl radical concentrations decrease.

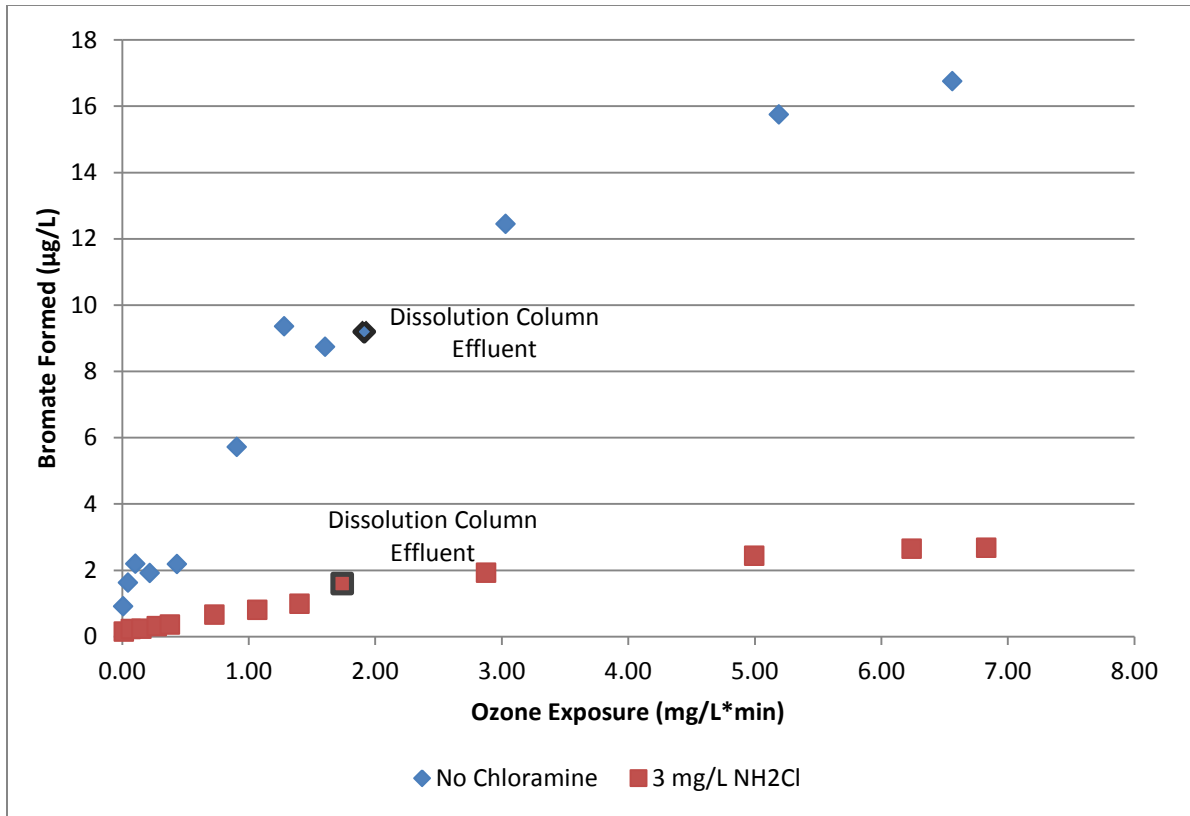


Figure 21- Bromate formed throughout the contactor with and without monochloramine

Wert, Rosario-Ortiz, and Snyder (2009) found that 68-77% of $^{\bullet}\text{OH}$ exposure occurred in the first 30 seconds at ozone doses of 0.8 to 1 $\text{O}_3:\text{TOC}$ in bench testing on three secondary effluents. This would explain the increased bromate formation rate in dissolution column. Despite the differences in mass transfer between bench testing and pilot and full-scale operation, final total ozone exposure could serve as a way to compare between scales.

In replicate testing considerable variability was observed. At the same ozone and monochloramine doses, ozone exposures varied by a factor of nearly five and bromate formation by six; data is summarized in Table 8.

Table 8- Water quality, ozone exposure, and bromate formation in replicate testing

Test #		1	2	3	4	5	6	7	8
Monochloramine	mg/L-Cl ₂	3	3	2.9	3	2.7	0	0	0
Ozone Dose	mg/L	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3
pH		7.16	7.18	7.24	7.24	7.34	7.42	7.09	7.07
Temperature	°C	13.8	14	14.2	14.2	15.6	13.2	14.6	14.3
Total Organic Carbon	mg/L	6.7	6.7	6.9	6.9	6.9	6.9	6.9	6.9
Alkalinity	mg/L-CaCO ₃	133	133	127	127	128	127	115	134
Ammonia	mg/L-N	0.8	0.79	0.8	0.8	0.87	0.11	0.16	0.28
Nitrite	mg/L-N	0.385	0.065	0.14	0.14	0.256	0.11	0.243	0.148
Bromide	mg/L	0.385		0.389	0.385	0.444	0.384	0.362	0.463
Dissolution Ozone Exposure	mg/L*min	1.04	0.84	1.74	2.05	1.35	1.91	1.27	0.77
Dissolution Bromate formed	µg/L	0.31	0.45	1.6	1.08	1.13	9.2	2.82	2.45
Total Ozone Exposure	mg/L*min	2.73	3.25	6.83	8.32	4.74	6.56	2.17	1.68
Final Bromate Formed	µg/L	0.4	0.823	2.68	2	1.54	16.75	3.82	3.79
Ozone Decay Rate	1/min	0.213	0.185	0.34	0.305	0.365	0.312	0.313	0.372
Comments		1st order decay curve did not trend back to highest point	Residual decay profile was not a good fit	Shown in figures 18, 20, & 21			Final bromate sample was not taken, exposure is calculated to the final residual point. Shown in figures 18, 19, 21		

Each of the water quality variables in Table 8 can change throughout the day during normal operation and effect ozone exposure and ^{*}OH generation indicating that total ozone exposure may not be the best measure to predict bromate formation in systems with variable water quality. TOC can lead to radical generation or act as a terminator, carbonate and bicarbonate act as radical scavengers. Increasing pH increases ozone decomposition into radicals and increases the reactivity of DOM with ozone. Temperature increases reaction rates which decrease ozone exposure. Weighing the effects of each is difficult and calls for detailed bench testing and development of a model.

4.4.4 Total Ozone Exposure and Bromate Formation at Varying Ozone and Monochloramine Doses

A matrix of tests were conducted at four ozone and monochloramine doses to better understand the relationship between ozone exposure, bromate formation and the effects of monochloramine on treatment and disinfection performance. The transferred ozone doses of 2, 3.5, 5.3, and 6.4 were chosen to roughly target O₃:TOC ratios of 0.25, 0.5, 0.75, and 1. These doses were used for an ongoing study on the effects of ozonation and chloramination on biofiltration. The actual normalized ozone doses were slightly lower as TOC in the flocculation-sedimentation effluent increased over the course of testing and ozone doses were not corrected for fluctuations in nitrite. Water quality for these tests is summarized in Table 9. The average total ammonia is skewed high due to high effluent ammonia, 3.7-5.5 mg/L-N, from the wastewater plant due to plant upset during a rain event on the day of the 1 mg/L NH₂Cl testing. Total ammonia ranged from 0.64 to 0.78 mg/L-N for the tests without monochloramine.

Table 9- Average water quality for total ozone exposure test matrix

TOC mg/L	pH	Temp °C	Total NH ₃ mg/L-N	NO ₂ mg/L-N	NO ₃ mg/L-N	Bromide mg/L
6.98	7.41	19.0	2.42	0.115	0.444	0.377

The lowest ozone dose of 2 mg/L was right around the IOD of the water, with a measurable residual being measured in the effluent of the dissolution column only some of the time. The highest measured residual was 0.07 mg/L and is insufficient for any disinfection credit. Figure 17 shows that in this condition, despite being what could be called a subresidual ozone dose, a slight measurable residual was present around the diffuser. This indicates that there is ozone exposure occurring at doses at or below IOD, it is just difficult to measure using traditional methods.

Ozone exposure in the dissolution column increased with increasing ozone dose but decreased as a portion of the total ozone exposure, which includes both the dissolution and contactor ozone exposure. Total ozone exposure increased exponentially with ozone dose as shown in Figure 22. This trend is consistent with bench results by Wert, Rosario-Ortiz et al. (2007). While the actual ozone exposures changed with monochloramine dose, the relationships between the ozone

exposures remained the same, with nearly 100% of the exposure occurring in the dissolution column for the lowest ozone dose and 10-30% for the highest.

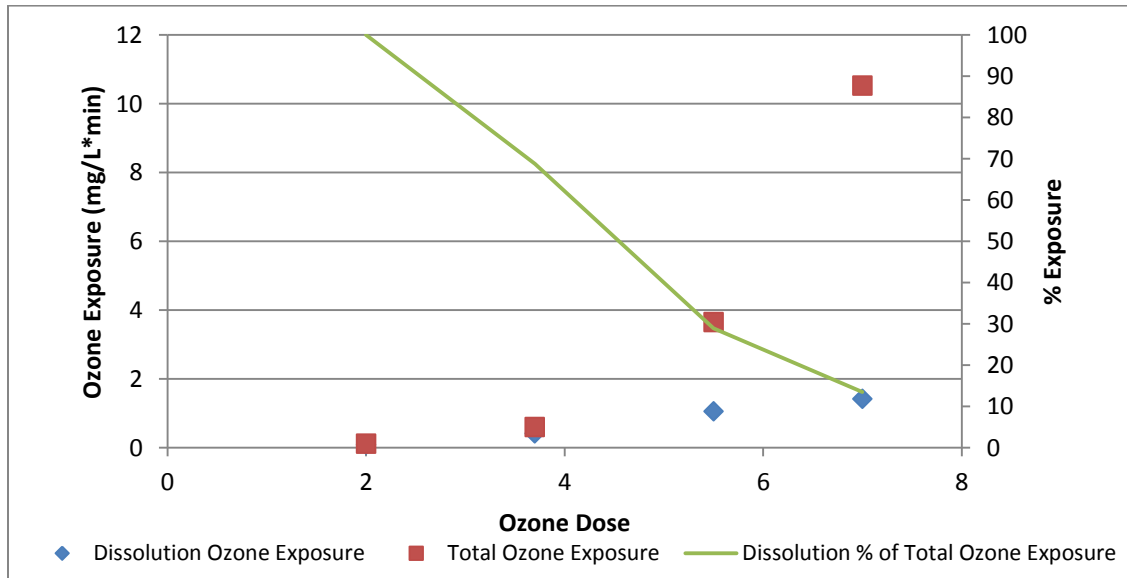


Figure 22- Dissolution and total ozone exposure for 0 mg/L NH₂Cl

During previous tests a decrease in ozone exposure was observed at higher monochloramine doses. Benotti et al. (2011) had to increase ozone dose by approximately 25% to achieve the same disinfection CT when using monochloramine. This was hypothesized to be due to monochloramine oxidation to nitrate. Figure 23 shows decreased ozone exposure at 5 mg/L NH₂Cl at the higher ozone doses. However, ozone exposure did not decrease proportionally with the other two monochloramine doses and this may be due to the variability in testing discussed earlier.

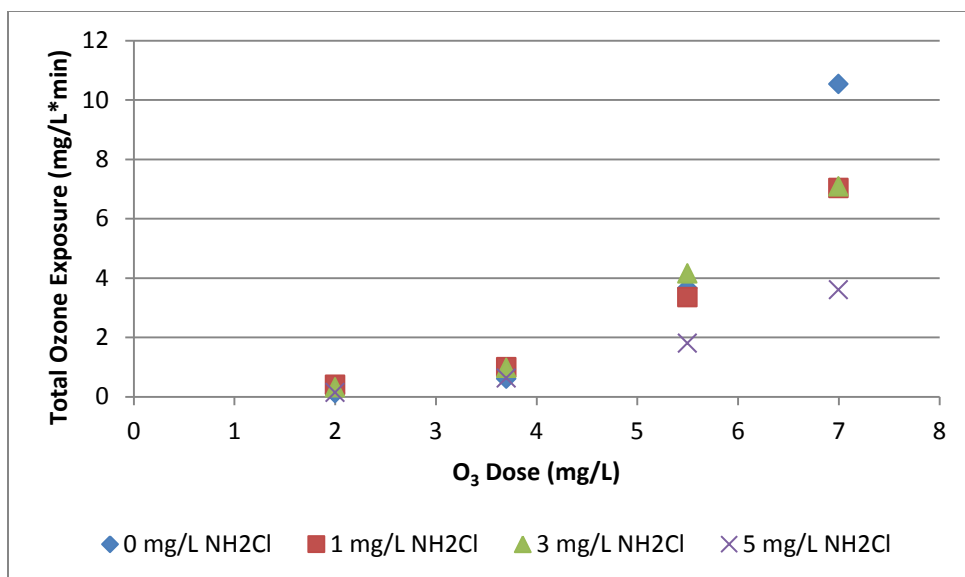


Figure 23- Total ozone exposure for varying ozone and monochloramine doses

Consistent with previous tests, monochloramine had little effect on initial ozone demand (IOD). However, there was a slight increase in IOD at the highest ozone and monochloramine dose as shown in Table 10. For this test ozone exposure both in the dissolution column and the contactor were lower. The only abnormal parameter was that the temperature was around 2.5°C higher than the other tests.

Table 10- Initial Ozone Demand (IOD)

Transferred O ₃ Dose (mg/L)	Monochloramine (mg/L-Cl ₂)				Average Percent of Dose
	0	1	3	5	
	Initial Ozone Demand (mg/L)				
1.96	1.95	1.89	1.92	1.94	98
3.56	3.27	3.2	3.1	3.19	90
5.26	4.21	4.02	4.01	4.16	78
6.42	4.6	4.71	4.53	5.35	75

4.4.5 Bromate Formation

Bromate appeared to increase linearly with ozone dose for all but the lowest dose (Figure 24). The bromate formed at 2 mg/L O₃ was minimal and did not follow any discernable pattern with monochloramine dose. Influent bromate samples were not taken for all tests, however, influent concentrations as high as 1.5µg/L have been seen before. A similar linear trend above the IOD was observed by Wert, Rosario-Ortiz et al. (2007). In prior testing bromate formation had been

extremely linear with ozone dose, though no tests were conducted below the IOD. Minimal hydroxyl radical generation occurs below 0.25 O₃:TOC. This is possibly due to reactions with olefins and tertiary amines which react quickly with ozone but do not produce large yields of O₂⁻ and O₃⁻ which lead to ^{*}OH production (Buffle & von Gunten, 2006; Chys et al., 2017; Lee & von Gunten, 2016). Due to the selective nature of ozone, ozone would be consumed by the most reactive forms of DOM before oxidizing bromide to bromate through the direct pathway.

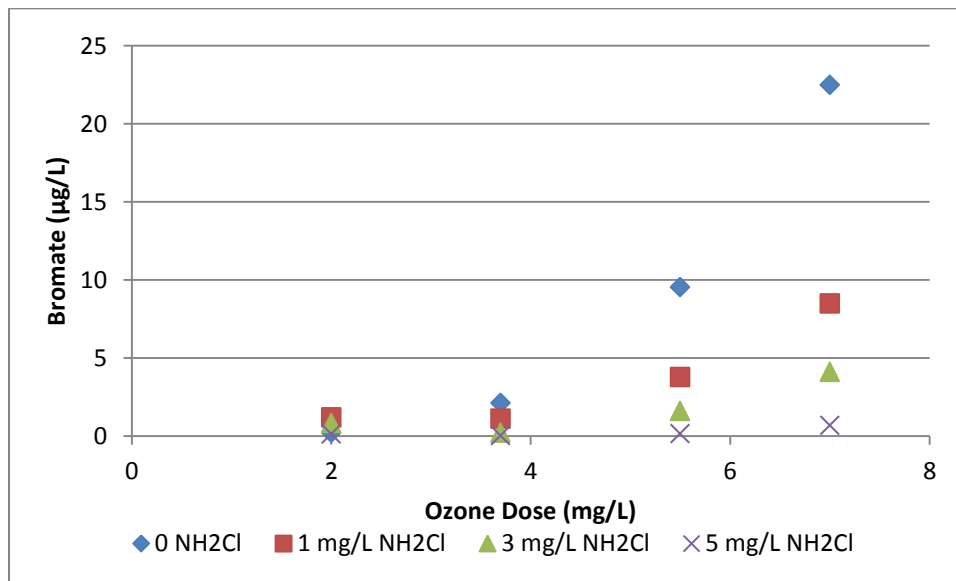


Figure 24- Bromate formed at varying ozone and monochloramine doses

Increasing monochloramine continued to decrease bromate. However, the 5 mg/L NH₂Cl results must be considered in respect to their lower ozone exposure. Interestingly, bromate was below the MCL for all but the highest ozone dose without monochloramine addition. During previous control tests, bromate had been greater than 10 µg/L for ozone doses as low as 3.5 mg/L. This could be due to lower bromide concentrations or the higher TOC increasing radical scavenging. When plotted against ozone exposure, a close to linear relationship is also formed (Figure 25). This is unexpected; as bromate formation is linear and exposure more exponential with ozone dose, when the two are compared bromate should increase by a power function. Bromate formation rate in the dissolution column and full contactor slows with monochloramine addition. Data is summarized in Table 11.

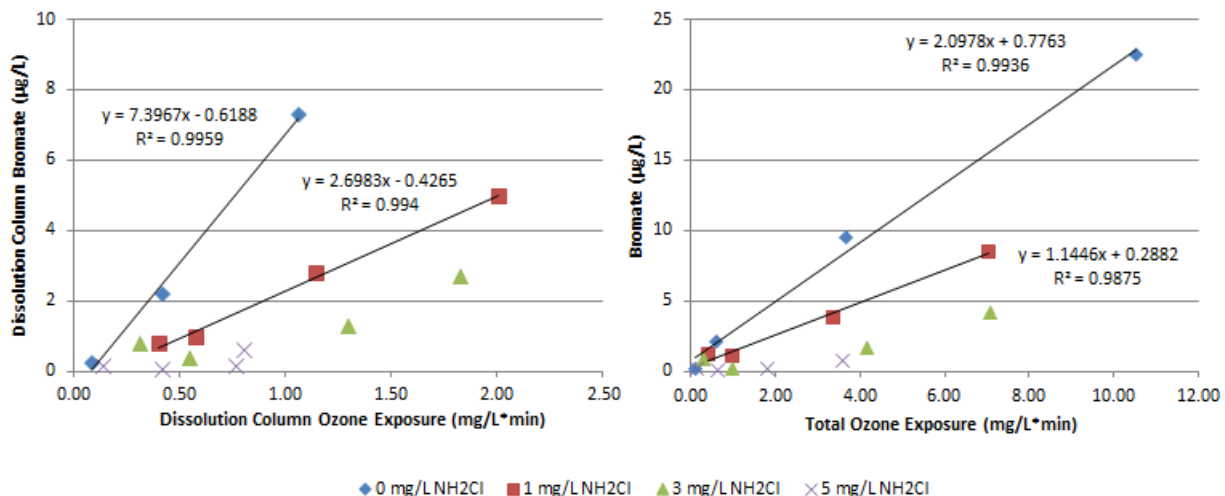


Figure 25- Ozone exposure and bromate formation in the dissolution column and final effluent

Table 11- Ozone Exposure and Bromate Formation Matrix Results

O ₃ Dose		Monochloramine (mg/L-Cl ₂)							
		0		1		3		5	
		O ₃ Exp mg/L*min	BrO ₃ µg/L	O ₃ Exp mg/L*min	BrO ₃ µg/L	O ₃ Exp mg/L*min	BrO ₃ µg/L	O ₃ Exp mg/L*min	BrO ₃ µg/L
1.96	Column	0.1	0.21	0.4	0.78	0.3	0.771	0.1	<i>0.116</i>
	Total	0.12	0.231	0.43	1.21	0.36	0.831	0.16	<i>0.131</i>
	% Column	75	91	93	64	87	93	83	89
3.5	Column	0.4	2.19	0.6	0.93	0.5	0.35	0.4	<i>0.038</i>
	Total	0.6	2.12	1.0	1.12	1.0	0.228	0.6	<i>0.039</i>
	% Column	69	103	58	83	56	154	67	97
5.3	Column	1.1	7.3	1.1	2.77	1.3	1.26	0.8	<i>0.131</i>
	Total	3.7	9.54	3.4	3.79	4.2	1.61	1.8	0.158
	% Column	29	77	34	73	31	78	43	83
6.4	Column	1.4		2.0	4.95	1.8	2.7	0.8	<i>0.577</i>
	Total	10.5	22.5	7.0	8.51	7.1	4.11	3.6	0.69
	% Column	14		29	58	26	66	22	84

Italicized values are raw results below the limit of quantification

For all tests the majority of bromate formed in the dissolution column, even at the highest ozone dose. This shows the importance of the higher ^{*}OH exposures occurring in the dissolution column. For the 5.3 mg/L O₃ dose the percentages of both ozone exposure and bromate formation occurring in the dissolution zone are similar across all NH₂Cl doses as discussed in

Section 4.4.3 with the more detailed tests. The same is presumably true for the other ozone doses but the data is inconclusive.

4.4.6 Sidestream Considerations

The other common method of ozone addition is sidestream injection. In this case a small stream is pulled off the main flow and ozone is added via a venturi injector before being mixed back in with the bulk flow. In sidestream without-degas systems, which are examined here, the gas bubbles remain in the sidestream flow until mixing with the bulk flow where gases release to the top of the contactor. In this case gas transfer occurs both in the sidestream and after mixing with the bulk flow in the contactor before degassing (Rakness et al., 2018). No disinfection credit is given for the sidestream ozone contact. However, if the sidestream is mixed in quickly, uncredited ozone exposure in the sidestream can be minimized.

Direct comparison was between sidestream injection and fine bubble diffusion was attempted on the pilot scale. However, several issues arose and the comparison was inconclusive. Gas transfer for the pilot sidestream was considerably lower than for bubble diffusion at the same ozone dose. Because there was no degassing on the sidestream before mixing back in with the remainder of the flow it was not possible to determine if gas transfer occurred at the venturi, throughout the sidestream, or at the mixing point. Gas to liquid ratios (G/L) tested ranged from 0.08 to 0.3, Wert et al., (2016) found that when $G/L > 0.1$ gas transfer occurred in both at the venturi and after mixing. Presumably with a 30s detention time some transfer is occurring in the sidestream after the venturi as well (Wert et al., 2016). High transfer efficiencies require higher pressures at the venturi inlet and higher ozone gas concentrations than were achievable on the pilot. Issues with coalescing bubbles and degassing at the sample ports made taking reliable residual ozone measurements difficult. If the sidestream could be made to work properly and transfer all gas at the venturi, it could be a very useful tool for understanding the nature of initial phase reactions. Despite these problems, conclusive bromate tests were able to be conducted, the results are presented in Figure 26. Bromate samples were taken from the sample ports along the sidestream prior to mixing back with the bulk flow.

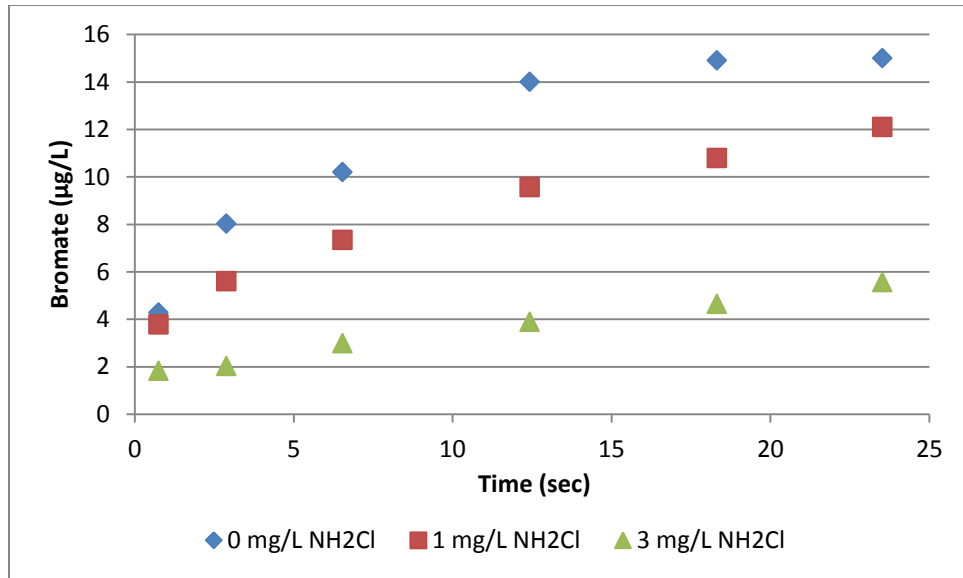


Figure 26- Bromate formed along the sidestream

Figure 26 shows the importance of minimizing sidestream detention time for bromate formation. Even at the first sample port 0.74 seconds downstream of the venturi there was significant bromate formation. These points may be skewed slightly high; samples were collected in 15mL centrifuge tubes with EDA for preservation and quenching which took approximately two seconds to fill and mix. Increasing monochloramine dose reduced final bromate formation as well as bromate formed in the first second. However, the bromate formed by the first sample port became a larger portion of the bromate formed in the sidestream so at higher chloramine doses there is less benefit in a shorter sidestream detention time. Typical design guidance is to try to keep detention time less than five seconds (Wert et al., 2016). With a detention time of >20s, initial phase reactions should be complete.

The other benefit of shortening the sidestream is minimizing ozone decay before mixing. Longer detention times will require additional ozone to meet oxidation and disinfection goals in the mixed flow and in turn create more bromate. In wastewater effluent, initial ozone decay is extremely fast. Buffle et al. (2006) found that around 50% of initial decay in the first 20 seconds had occurred in less than 350 milliseconds when using a quench flow system to measure ozone decay in secondary effluent. In this case, substantial ozone decay would still occur in any sort of practical length of sidestream. One of the primary operational benefits of sidestream injection is that the ozone gas feed and injection can be contained in a separate room for serviceability and

safety. In order to minimize sidestream ozone decay and bromate formation this may not be possible.

If the observations on IOD in bubble diffusion from Table 10, where demand decreases as a fraction of dose, hold true for sidestream systems sidestreams should be operated as close to the highest possible ozone dose to minimize ozone lost to decay in the sidestream. However, this requires careful sizing of the ozonation system and provides less operational flexibility for increased demand due to variable influent characteristics such as nitrite or overfeeding of methanol. In order to transfer higher ozone doses to the sidestream, higher venturi pressures may be required which increase pumping costs. Sidestream injection is often more expensive than bubble diffusion but more practical to operate (Rakness et al., 2018). If bromate formation is not a concern, trying to minimize ozone wasted to sidestream decay and transfer efficiency may be more expensive than increasing ozone dose.

4.4.7 Disinfection Credit

Ozone has been shown to be effective for the inactivation of viruses, *Giardia*, and *Cryptosporidium* which are key disinfection requirements for drinking water treatment. In direct or indirect potable reuse scenarios it serves as part of the multi-barrier approach to protection against pathogens. Disinfection credit is awarded based on the ozone exposure or CT, concentration x time, measured in the disinfection zone of the contactor. CT is not measured in the dissolution zone in either bubble diffusion or sidestream injection. In fine bubble diffusion systems, 1-log virus credit is given if the ozone residual is greater than 0.1 mg/L in the effluent of the diffusion chamber and 0.5-log *Giardia* credit if the residual is greater than 0.3 mg/L. No *Cryptosporidium* credit is given for the diffusion chamber (EPA, 2010). No disinfection credit can be claimed in the sidestream, CT begins immediately after mixing with the bulk flow.

In the testing discussed above (section 4.4.5), ozone exposures up to 2 mg/L*min were observed in in the dissolution column, this is sufficient for 15-log virus and 0.5-log *Crypto* credit, only 1-log virus credit would have been awarded because the effluent residual was greater than 0.1 mg/L. Even at the lowest dose of 2 mg/L, there was enough measurable exposure around the diffuser for 2 to 3-log virus credit. However, no disinfection credit would have been awarded

under current guidelines. Figure 27 breaks down the achievable Virus log-reduction value (LRV) achievable at each ozone dose at 3 mg/L-Cl₂ NH₂Cl.

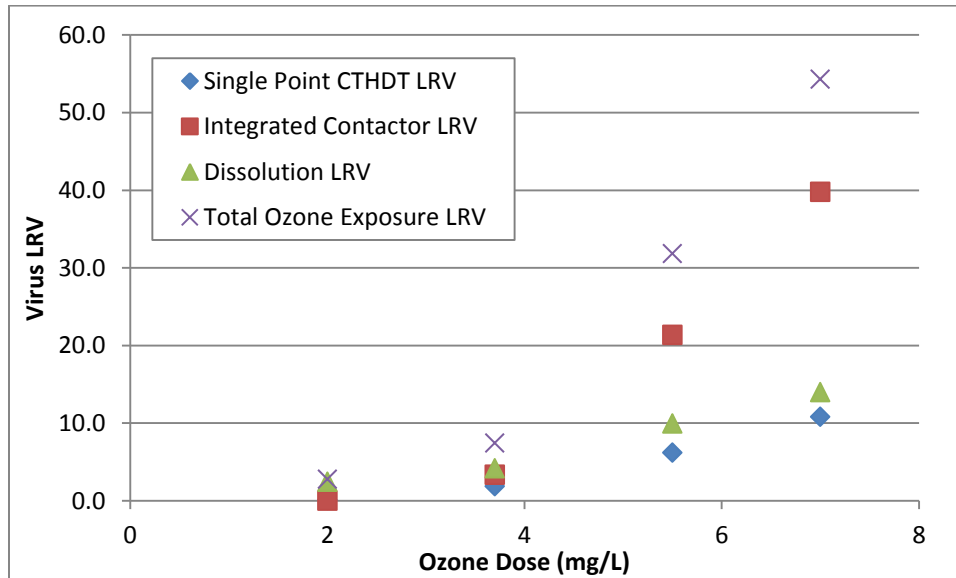


Figure 27- Achievable virus LRVs based on ozone exposure for 3 mg/L NH₂Cl

In some locations, including the state of Virginia, CT determination is based around only a single residual ozone concentration at a known hydraulic detention time. This is shown as the single point CT_{HDT} LRV in Figure 27. This method is extremely conservative. For all doses the single point LRV was lower than the uncredited LRV in the dissolution column. It is clear that there is a large portion of uncredited CT occurring in the dissolution zone. By minimizing uncredited dissolution exposure, ozone doses can be lowered and bromate decreased.

As mentioned before, the 4.2 minute detention time of the pilot dissolution column is extremely long and represents turndown conditions. With this long detention time ozone exposure, ozone decay, and bromate formation are occurring before the disinfection zone. This can be minimized both in operation and design. During turndown conditions, parallel contactors can be taken out of service to increase flow and decrease detention time (Wert et al., 2017). Minimizing bubble diffusion chamber detention time should be emphasized when designing contactors, though it does require balance: current guidelines state that the diffusion chamber must be the same size or larger than the downstream chambers in order to get the 1-log virus and 0.5-log *Giardia* credit. To reduce decay in the dissolution zone a smaller diffusion chamber might be used but these

disinfection credits would be lost (EPA, 2010). At some point ozone transfer becomes limited (Wert et al., 2016). There may also be issues with spacing of diffusers in a smaller chamber, especially with the higher ozone doses used in wastewater reuse (A. Newbold, personal communication, September 21, 2018).

For sidestream systems minimizing detention time and decay allows a higher ozone dose to be applied in the compliance zone. Therefore disinfection goals to be met at a lower ozone dose and bromate formation will be reduced.

4.5 CONCLUSIONS

This study set out to examine the effects of ozone exposure and dissolution methods on bromate formation and control in high bromide reuse waters. Direct comparison between the two ozone dissolution methods was not possible due to pilot testing issues, however, some insight into the effects of dissolution methods on bromate formation were drawn.

- For fine bubble diffusion systems, considerable ozone exposure and bromate formation can occur in the dissolution chamber. Dissolution zone bromate formation correlates well with ozone exposure. However, due to the high *OH concentrations in the initial phase of ozonation, bromate forms at a faster rate.
- Even at low, sub-residual ozone doses there is a slight measurable ozone residual around the diffuser. At 2 mg/L O_3 there was enough ozone exposure for two to three-log virus credit yet no disinfection credit would have been awarded by current guidelines.
- Monochloramine addition slowed bromate formation in both the dissolution column and the main contactor. Bromate was kept below the MCL at the highest transferred ozone dose of 6.3 mg/L with 1 mg/L of added NH_2Cl , increasing dose continued to reduce bromate concentrations.
- The decrease in bromate formation in the dissolution column indicates that monochloramine is acting as a hydroxyl radical scavenger. During the initial phase of ozonation, more bromate is formed through the indirect pathway via hydroxyl radicals. Masking $HOBr$ as NH_2Br does not limit bromate formed through this pathway.
- In both sidestream injection and bubble diffusion, minimizing detention time is critical to reduce bromate formed in the dissolution zone. Shorter detention times also reduce ozone

decay and allow a higher initial residual to enter the contactor. This allows disinfection CT goals to be met at a lower ozone dose, reducing bromate formation and operating costs.

- Ozone exposure may not be a good measure to predict bromate formation in systems with variable water quality. TOC, alkalinity, pH, and other parameters influence the relative amount of hydroxyl radical generation and scavenging.

4.5.1 Future work and methods discussion

Throughout the testing in this manuscript and the first manuscript, inexplicable variability was often observed. For the testing in Section 4.4.3, where bromate and ozone exposure varied by five or six times in replicate testing, there was no reasonable explanation based on TOC, temperature, pH or other simple to monitor water quality factors. Several weeks after these tests were completed, the mass flow controller, which regulates the gas flow rate and is part of the applied ozone dose calculation, failed due to unknown contamination issues. Perhaps the mass flow controller had not been functioning properly for some time before it failed and the applied doses reported were not correct. In the previous testing (Manuscript 1), ozone decay in the contactor had followed nearly perfect first order decay, $R^2 > 0.94$ for all but one test where ozone residuals were measured. In these tests, however, the fit was not always as good. Samples were not taken at detention time so if the applied dose was fluctuating significantly this might have been caught in these residual profiles. The matrix of tests in Sections 4.4.4 & 4.4.5 was conducted following the replacement of the mass flow controller. However, the bromate data (Table 11) is not very consistent, in several cases the bromate measured at the outlet of the dissolution column was greater than the final effluent bromate. Due to the time constraints of moving the pilot from York River Treatment Plant to the SWIFT Research Center at Nansemond Treatment Plant, the bromate samples had not been analyzed. Therefore it was not possible to replicate the tests on the same water.

Without hydroxyl radical data the discussion on demand in the bubble diffusion column is all very hypothetical (Section 4.4.1). It is difficult to quantify how much ozone was consumed by the water matrix in the top of the column. Adding a probe compound, which is only degraded by

hydroxyl radicals, in order to measure the hydroxyl radical exposure on the pilot scale could be difficult. While UV 254 change was used as a surrogate for hydroxyl radical exposure in Manuscript 1, it is possible that change at higher wavelengths, 270-285 nm may be better correlated with ozone exposure (Audenaert et al., 2013; Buffle et al., 2006). If a suitable quenching agent for ozone could be found that does not interfere at the desired wavelengths, these measurements may help understand what is occurring in the diffusion column.

UV absorbance measurements may also be useful to understand the ozone *consumed* rather than just ozone exposure. As discussed above, many water quality parameters can change and hydroxyl radical exposure. Temperature effects most reaction rates and thus changes ozone exposure relative to $^{\bullet}\text{OH}$ exposure though it is not really a measure of the *quality* of the water. Looking at changes in the UV absorbance spectra could provide more meaningful and adaptable measure than ozone exposure.

5 ENGINEERING SIGNIFICANCE

As the need for water reuse increases, ozonation can serve as part of a more cost effective treatment process than traditional membrane based techniques. However, the formation of bromate as a byproduct of the ozonation of bromide can be a major hurdle to overcome in order to meet drinking water standards. Preformed monochloramine can successfully be used to control bromate formation to below the MCL of 10 µg/L in reuse waters with bromide concentrations of 500 µg/L or greater. Monochloramine appears to act as a hydroxyl radical scavenger which makes it particularly applicable for wastewater ozonation which generates higher ^{*}OH concentrations than natural source waters in drinking water treatment.

Beyond a certain point additional monochloramine had little effect on improving bromate suppression. This point of diminishing return is likely water quality dependent, but what exactly that is needs to be studied further. Hydroxyl radical scavenging continues to increase with increasing monochloramine dose, while bromate suppression levels off. Overdosing monochloramine for a factor of safety may negatively impact oxidation through ^{*}OH and decrease disinfection credit by increasing ozone decay rate and decreasing exposure. Additionally this increases chemical dosing costs both for monochloramine and a quenching agent prior to biofiltration with little treatment benefit.

The effects of radical scavenging on AOC generation require further investigation. Biofilter TOC removal increased with increasing ozone dose. With monochloramine, higher ozone doses are achievable while controlling bromate. In treatment trains with GAC as a downstream polishing step, including HRSD's SWIFT process, removing additional TOC through biofiltration could free up additional adsorptive capacity for trace organics and decrease carbon regeneration frequency.

Significant bromate can form in the dissolution zone where no disinfection credit is awarded for both fine bubble diffusion and sidestream injection systems. Dissolution systems and contactors should be designed in order to minimize ozone exposure and decay in the dissolution zone so that disinfection objectives can be met at lower ozone doses. Unlike ammonia addition alone and

pH suppression, monochloramine can reduce bromate formed in the initial phase of ozonation that occurs in the dissolution zone.

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APPENDIXES

Appendix A-Bromide Spike Testing

For this test, sodium bromide was spiked into the ozone influent in order to see the relationship between bromide and bromate formation at a constant ozone dose. Tests were run over several hours to minimize the effects of day to day variation in other water quality parameters. The applied ozone dose was set at 5.5 mg/L (~0.75 O₃:TOC) and 3 mg/L NH₂Cl was added, this was the typical operating condition for testing during this period.

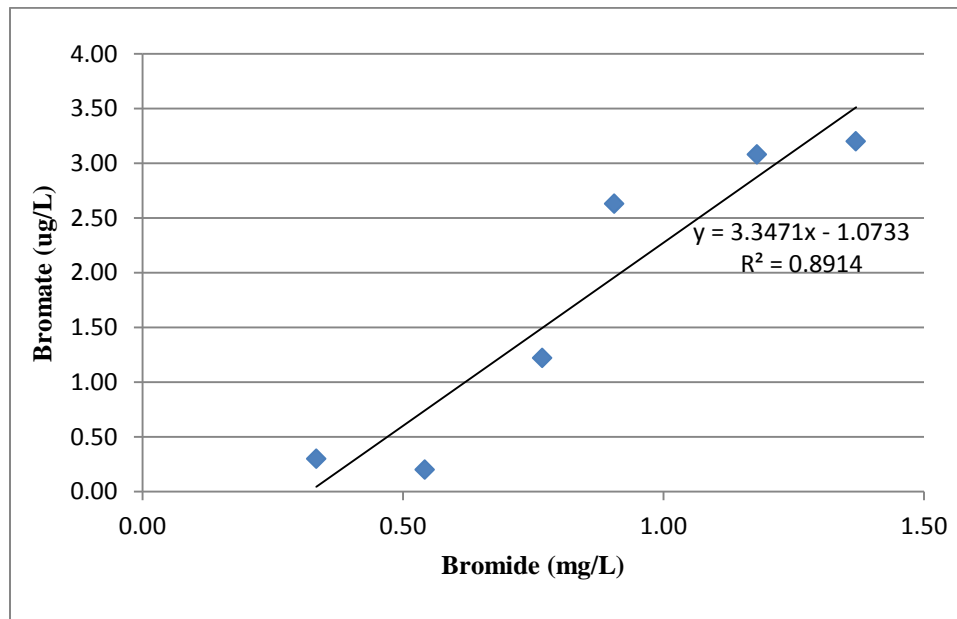


Figure 28- Bromide v. Bromate at 5.5 mg/L O₃ and 3 mg/L NH₂Cl

Table 12- Bromide Spike Test Results

Bromide mg/L	Bromate µg/L
0.33	0.30
0.54	0.20
0.77	1.22
0.91	2.63
1.18	3.08
1.37	3.20

Bromate formation correlated well with bromide concentration. 5.5 mg/L of O₃ was sufficient for 3-log virus credit and bromate was safely below the MCL at bromide concentrations up to 1.37 mg/L. This is very promising for future plants with high influent bromide which wish to use ozonation without excessive chemical doses for bromate suppression or ion exchange to remove bromide.

Appendix B- Monochloramine and UV254 Absorbance

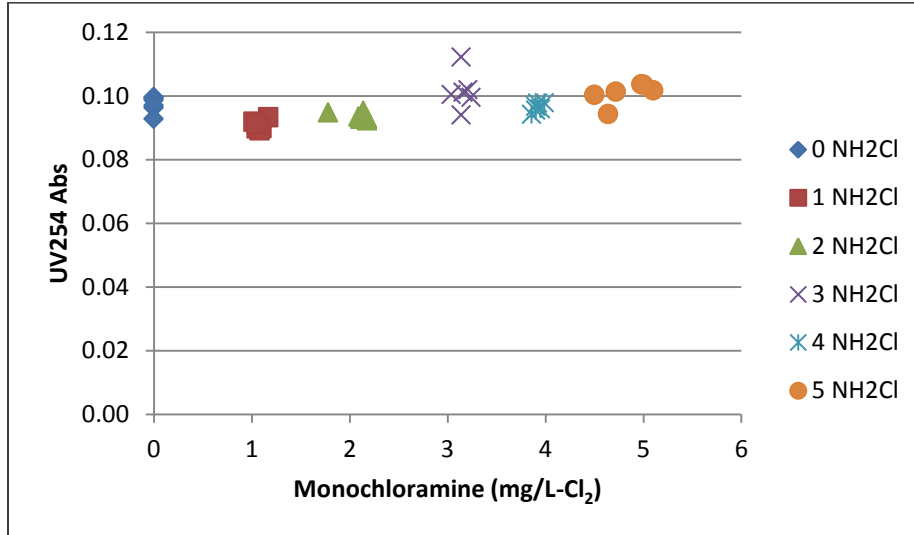


Figure 29- Initial UV 254 absorbance with monochloramine present

Monochloramine did not appear to interfere on UV absorbance measurements at 254 nm taken prior to ozonation.

Appendix C- LRV Calculations

Virus log removal values were calculated using the following equations which interpolate off Table C-13 from the EPA Disinfection Profiling and Benchmarking Guidance Manual (EPA, 1999).

$$\text{Estimated Virus LRV} = 4.0 \times (\text{CT}_{\text{actual}} / \text{CT4 LRV Virus})$$

$$\text{For temp. } \leq 5^{\circ}\text{C CT4 LRV, Virus} = (-0.15 \times \text{Temp}) + 1.95$$

$$\text{For } 5^{\circ}\text{C} < \text{temp. } \leq 10^{\circ}\text{C CT4 LRV, Virus} = (-0.04 \times \text{Temp}) + 1.4$$

$$\text{For } 10^{\circ}\text{C} < \text{temp. } \leq 15^{\circ}\text{C CT4 LRV, Virus} = (-0.08 \times \text{Temp}) + 1.8$$

$$\text{For } 15^{\circ}\text{C} < \text{temp. } \leq 20^{\circ}\text{C CT4 LRV, Virus} = (-0.02 \times \text{Temp}) + 0.9$$

$$\text{For temp. } > 20^{\circ}\text{C CT4 LRV, Virus} = (-0.04 \times \text{Temp}) + 1.3$$

Where $\text{CT}_{\text{actual}}$ is the measured CT based on the measured ozone residual, C, times the known detention time, T, of the sample port times a baffle factor. A baffle factor of 0.7 was used for the pilot.

An additional 1-log virus credit was added to the Estimated Virus LRV when ozone concentrations were greater than 0.1 mg/L at the effluent of the dissolution column.

Appendix D- Maximizing CT and LRV for a single residual point

When using a single ozone residual sample point to determine CT for disinfection, the measured CT can vary significantly depending on when CT is determined. For this example it is assumed that ozone decay in the contactor is perfectly first order per equation XXXX.

$$C = C_0 e^{-kt}$$

Where C is the ozone concentration in mg/L at any point in the contactor, C_0 is the concentration at time zero, and k is the pseudo first order ozone decay rate in min^{-1} .

Therefore $CT = C * t * \text{Baffle Factor} = C_0 e^{-kt} * t * \text{Baffle Factor}$. The derivative can be taken and zeros found to find the maximum CT.

$$CT = C_0 e^{-kt} * \text{Baffle Factor} * t$$

$$\frac{d(CT)}{dt} = BF * C_0 \left((e^{-kt} * -k) + (1 * e^{-kt}) \right)$$

$$\frac{d(CT)}{dt} = BF * C_0 (e^{-kt}(-kt + 1))$$

$$0 = BF * C_0 (e^{-kt}(-kt + 1))$$

$$0 = e^{-kt}(-kt + 1)$$

$$0 = -kt + 1$$

$$t = 1/k$$

$$0 = e^{-kt}$$

$$\ln 0 = -kt$$

$$t \neq 0$$

The maximum CT occurs $t=1/k$, this can also be verified using real data. Figure 30 shows a set of ozone decay curves collected during testing for Manuscript 1. Table 13 was generated by applying Equation xxxx to the trend line equations in Figure 30.

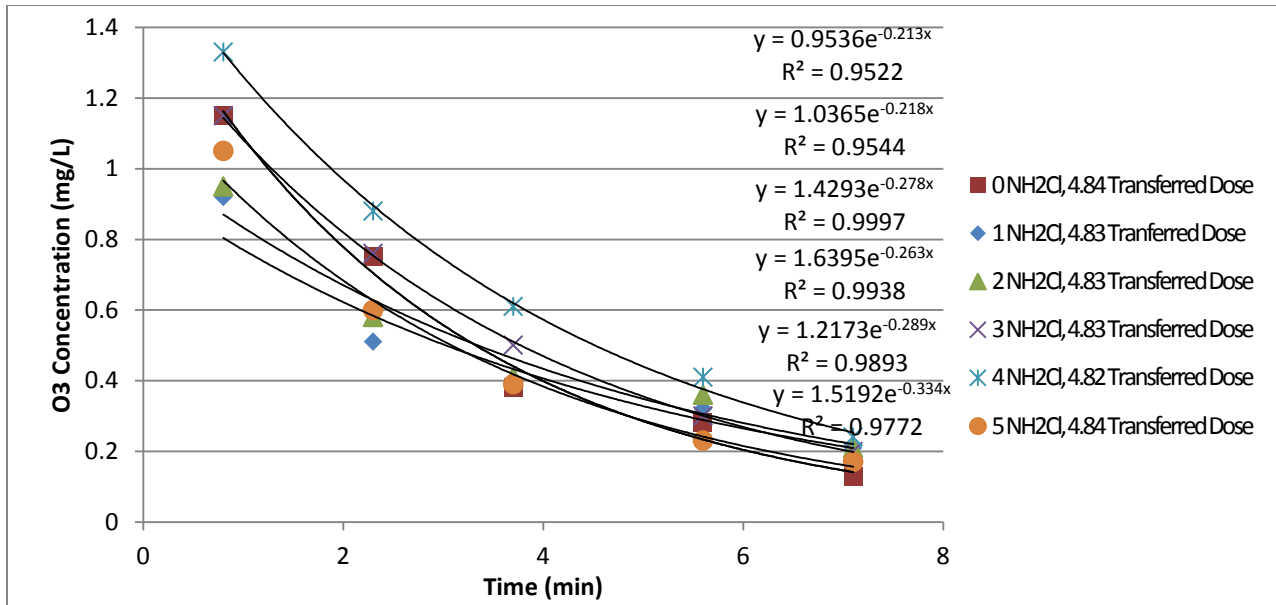


Figure 30- Ozone decay curves for 0.75 O₃:TOC at varying NH₂Cl dose

Table 13- Calculated CT over time for 0.75 O₃:TOC decay curves

Monochloramine	0	1	2	3	4	5
Co (mg/L)	0.954	1.037	1.429	1.640	1.217	1.519
k (1/min)	0.213	0.218	0.278	0.263	0.289	0.334
Time (min)	CT (mg/L*min)					
1.00	0.54	0.58	0.76	0.88	0.64	0.76
1.50	0.73	0.78	0.99	1.16	0.83	0.97
2.00	0.87	0.94	1.15	1.36	0.96	1.09
2.25	0.93	1.00	1.20	1.43	1.00	1.13
2.50	0.98	1.05	1.25	1.49	1.03	1.15
2.75	1.02	1.10	1.28	1.53	1.06	1.17
3.00	1.06	1.13	1.30	1.56	1.07	1.17
3.25	1.09	1.16	1.32	1.59	1.08	1.17
3.50	1.11	1.18	1.32	1.60	1.08	1.16
3.75	1.13	1.20	1.32	1.61	1.08	1.14
4.00	1.14	1.21	1.32	1.60	1.07	1.12
4.25	1.15	1.22	1.30	1.60	1.06	1.09
4.50	1.15	1.22	1.29	1.58	1.04	1.06
5.00	1.15	1.22	1.25	1.54	1.00	1.00
5.50	1.14	1.20	1.19	1.49	0.96	0.93
6.00	1.12	1.18	1.13	1.42	0.90	0.86
7.00	1.05	1.10	1.00	1.27	0.79	0.72
8.00	0.97	1.01	0.87	1.12	0.68	0.59
9.00	0.88	0.92	0.74	0.97	0.57	0.47
Max CT	1.15	1.22	1.32	1.61	1.08	1.17
Time of Max CT	4.5	4.5	3.5	3.75	3.5	3.0
1/k (min)	4.69	4.59	3.60	3.80	3.46	2.99

The maximum calculated CT in Table 13 occurs close to the time predicted by $1/k$. The true maximum is not captured because of the resolution of the time scale in 0.25 minute increments. The measured CT for the same ozone residual curve can vary by a factor of two depending on where the sample is taken. By taking the residual for disinfection compliance at the optimum time, disinfection goals could be met at lower ozone doses or a factor of safety on measured LRVs could be ensured.