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Evaluation of preformed monochloramine for bromate control in ozonation for potable reuse

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ABSTRACT

Bromate, a regulated disinfection byproduct, forms during the ozonation of bromide through reactions with both ozone and hydroxyl radical. In this study, preformed monochloramine was evaluated for use as a bromate suppression method in pilot testing of wastewater reuse with an average bromide concentration of 422±20 μg/L. A dose of 3 mg/L NH_2Cl-Cl_2 decreased bromate formation by an average of 82% and was sufficient to keep bromate below the MCL at ozone doses up to 8.6 mg/L (1.2 O_3:TOC). Removal of 1,4-dioxane through ozonation decreased with increasing NH_2Cl dose, confirming that monochloramine suppresses bromate formation, at least in part, by acting as a hydroxyl radical scavenger. This may negatively impact oxidation objectives of ozonation in reuse applications. Increasing monochloramine contact time did not improve bromate suppression, indicating that monochloramine probably did not mask bromide as NHBrCl or other haloamines prior to ozonation. However, NHBrCl and NH_2Br may be formed from reactions between HOBr and NH_2Cl and excess free ammonia during ozonation. NDMA was formed by ozonation at concentrations up to 79 ng/L and was not enhanced by NH_2Cl addition.

1. Introduction and background

Ozonation coupled with biofiltration has recently emerged as a promising alternative to membrane-based processes for potable reuse applications. This process offers significant cost savings in terms of 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., 2014). In this process ozone provides bulk organics degradation, assimilable organic carbon (AOC) generation, and transforms trace organic contaminants (TOrCs) into more readily biodegradable transformation products, while also providing a barrier against pathogens (Arnold et al., 2018; Knopp et al., 2016; Reungoat et al., 2012; Wert et al., 2007).

Ozone is a powerful oxidant which also leads to the generation of hydroxyl (*OH) and other radicals through reactions with dissolved organic matter (DOM). Hydroxyl radical is nonselective and extremely fast reacting. While transient concentrations and exposures are very low, it is considered the strongest oxidant available for water treatment. Ozone decomposition follows multiphasic kinetics; in the initial phase ($t < \sim 30$ s) rapid ozone decomposition takes place due to fast direct reactions with organics that generate large amounts of *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 can generate hydroxyl radical concentrations greater than those found in advanced oxidation process (AOP) applications in natural waters (Buffle et al., 2006).

Bromate (BrO_3^-) is formed through the ozonation of bromide containing waters and is the primary disinfection byproduct (DBP) of ozonation. A maximum contaminant level for bromate of 10 μg/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 μg/L (von Gunten, 2003b). Bromate is formed through a complex series

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of both ozone and hydroxyl radical reactions (Fig. 1) (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 radical to form BrO* 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 and is likely responsible for much of the bromate formation in wastewater ozonation. In this pathway, bromide is radicalized by *OH, 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; Soltermann et al., 2017).

There are several common chemical bromate control strategies. pH suppression shifts the $HOBr/OBr^-$ equilibrium towards hypobromous acid, thus decreasing bromate formation through the direct pathways as well as possibly decreasing *OH generation. Hydrogen peroxide addition rapidly converts ozone into *OH, decreasing overall ozone exposure and can also catalytically reduce hypobromous acid (von Gunten and Oliveras, 1998). Ammonia can be added to form bromamine (NH_2Br) from hypobromous acid which masks bromide from further oxidation (Table 1 Reaction 1). In the chlorine-ammonia process, free chlorine is used to pre-oxidize bromide to hypobromous acid then ammonia is added to mask bromide as NH_2Br prior to ozonation. Monochloramine may also be formed from excess free chlorine and acts as a radical scavenger (Table 1 Reaction 3), as such the NH_3-Cl_2 has also been used to control bromate. Hydroxyl radical scavenging was hypothesized to be the primary benefit of monochloramine over ammonia addition alone (Buffle et al., 2004). Similar to ammonia, monochloramine can react with HOBr to form bromochloramine, NHBrCl (Table 1 Reaction 2). Recently Ling et al. (2020) claimed that bromochloramine and dibromamine, $NHBr_2$, were formed prior to ozonation (Table 1 Reactions 4 and 5) in the NH_3-Cl_2 process. Six minutes of monochloramine contact time was provided to mask the majority of bromide as NHBrCl and $NHBr_2$. These compounds were also found to be more resistant to ozonation than NH_2Br.

Hampton Roads Sanitation District's (HRSD) SWIFT Research Center (SRC) is a 3.8 MLD demonstration scale advanced water treatment facility located in Suffolk, Virginia. The facility treats secondary effluent from the Nansemond Treatment Plant (5-stage Bardenpho process with methanol addition) to drinking water standards for recharge into the Potomac Aquifer. The treatment train consists of coagulation, flocculation, and sedimentation followed by ozonation, biofiltration, granular activated carbon adsorption, and UV disinfection. The facility also houses a similarly configured pilot scale (4 L/min) treatment plant for experimental work. Due to the low lying, coastal nature of HRSD's collection system, bromide concentrations of 400 μg/L or higher are often present due to saltwater infiltration as well as specific industrial sources such as landfill leachate.

Table 1

Relevant reactions for bromate suppression by monochloramine.

Reaction	Rate Constant	Citation	Number
$HOBr + NH_3 \rightarrow NH_2Br$	$k = 7.5(10^7)\ M^{-1}s^{-1}$	Wajon and Morris (1982)	(1)
$HOBr + NH_2Cl \rightarrow NHBrCl$	$k = 2.86(10^5)\ M^{-1}s^{-1}$	Gazda and Margerum (1994)	(2)
$NH_2Cl + {}^*OH \rightarrow NHCl^*$	$k = 5(10^8)\ M^{-1}s^{-1}$	Poskrebyshev et al. (2003)	(3)
$2\ NH_2Cl + Br^- \rightarrow NHBrCl + NH_3 + Cl^-$	$k = 3.54(10^6)\ M^{-2}s^{-1}$ at pH 7	Trofe et al. (1980)	(4)
$2\ NHBrCl + Br^- \rightarrow NHBr_2$	$k = 565\ M^{-1}s^{-1}$	Luh and Mariñas (2014)	(5)
$O_3 + NH_2Cl \rightarrow NO_3^- + Cl^- + H^+$	$k = 26\ M^{-1}s^{-1}$	Haag and Hoigné (1983)	(6)

During initial testing, pH suppression was found to be impractical on the pilot scale and cost prohibitive for full scale implementation due to the high alkalinity in the wastewater effluent (data not shown). Hydrogen peroxide was not considered due to the project requirement to achieve an ozone residual for disinfection CT credit. Ammonia addition was tested briefly but could not effectively keep bromate below the MCL (Buehlmann et al., 2017). Preformed monochloramine, where monochloramine is formed using sodium hypochlorite and ammonium sulfate fed into softened carrier water, was selected for bromate control. This was chosen due to the ease of control and decreased chemical demand over the NH_3-Cl_2 or Cl_2-NH_3 with somewhat variable NH_4^+ and NO_2^-in the wastewater effluent, and the desire to minimize production of free chlorine DBPs (when NH_4^+ is low). Preformed monochloramine also decreases the possibility of n-Nitrosodimethylamine (NDMA) formation by dichloramine (Hogard et al., 2021; Mitch et al., 2005; Schreiber and Mitch, 2005).

Of particular concern is 1,4-dioxane, a trace contaminant and potential human carcinogen commonly found in wastewater effluents due to its use in industry and household supplies such as detergents (Tanabe and Kawata, 2008). Influent concentrations typically range from 0.5 to 1 μg/L at the SWIFT Research Center and it has a 10^{-6} lifetime cancer risk associated with a concentration of 0.35 μg/L (EPA, 2013). It is not readily biodegradable or well adsorbed and through ozonation it is only removed by *OH oxidation, in which case radical scavenging by NH_2Cl may decrease its removal (Hogard et al., 2021).

The objectives of this study were to determine the efficacy of preformed monochloramine for bromate control during ozonation of a high bromide reuse water. Secondary effects of monochloramine addition on *OH exposure, ozone demand, decay, and disinfection credit were also analyzed as well as NDMA formation through ozonation. While determining the mechanisms of bromate suppression by monochloramine was not the objective of this study, results and the implications on treatment performance were analyzed in light of these mechanisms.

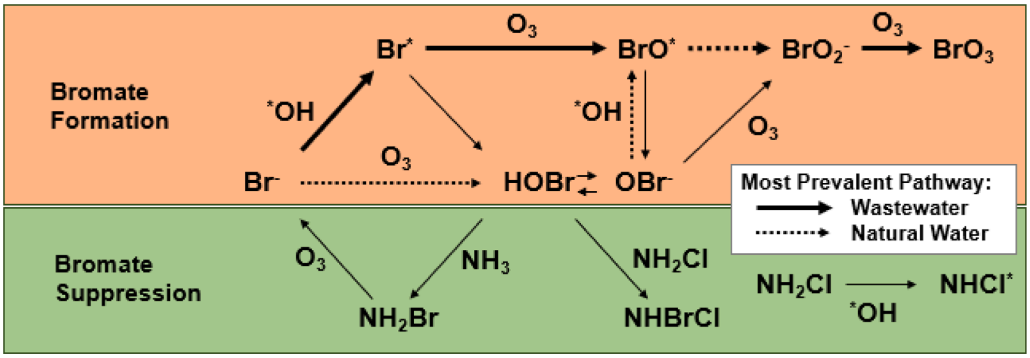

Fig. 1. Bromate formation pathways and suppression mechanisms. After Pinkernell and von Gunten (2001).

2. Materials and methods

2.1. Plant description

Pilot tests were conducted at HRSD's SRC at the Nansemond Treatment Plant (Suffolk, VA). Nansemond Treatment Plant is a 114 MLD (30 MGD), fully nitrifying and denitrifying plant utilizing a 5-stage bardenho treatment process with methanol addition for denitrification. 3.8 MLD (1 MGD) of the secondary clarifier effluent is fed into the SRC. The treatment train includes coagulation, flocculation, and sedimentation, followed by ozonation, biofiltration, granular activated carbon adsorption, and UV disinfection prior to deep well aquifer recharge. The plant operation has been described extensively elsewhere (Hogard et al., 2021).

Settled water from the SRC was fed to a pilot feed tank with a chiller to control the temperature to 20±0.8 °C, however for each test temperature stayed within a 1 °C range. Influent water quality is summarized in Table 2. A pipeline chloramine contactor was used upstream of the ozonation pilot to test the effects of monochloramine contact time as shown in Figure 2. The ozone pilot used was a modified Intuitech 2nd generation ozone pilot (Intuitech Inc, Salt Lake City, USA) operated at 3.94 L/min. The pilot ozone contactor consisted of one counter current dissolution column with a retention time of 1.5 min, followed by five contact columns also with a retention time of 1.5 min each. Each of the contact columns had a series of sample ports to measure ozone residuals along the contactor. Ozone was generated from oxygen from the onboard oxygen concentrator. Ozone gas concentrations ranged from 3.4 to 9.8% (w/w) as the lowest ozone doses required the gas flow rates to be increased for the oxygen/ozone mass flow controllers to control the dose well. Measured ozone transfer efficiency was >99%. However, in the above configuration the gas flow rates (0.15–0.3 SLPM) were below the optimal gas flow rates for the off gas analyzer. In previous testing with higher gas flow rates and lower gas concentrations, transfer efficiency was still typically >95%. Applied ozone doses were selected by taking a grab-sample for TOC and nitrite and adjusting the dose for the desired O_3:TOC ratio, all O_3:TOC ratios referenced herein are nitrite corrected. A TOC sample was also collected and sent to HRSD's Central Environmental Laboratory at the beginning of each test, the grab samples on the online instrument (Shimadzu TOC 4200) were found to read slightly higher than the laboratory instrument so the lab values were used. Influent UV absorbance changed by less than 5% over the course of each testing day so TOC was assumed to be constant for each test. Fig. 2

Preformed monochloramine stock was collected from the preformed monochloramine system at the SRC. In this system tap water is fed through GAC to dechlorinate and remove TOC which then followed by softening via ion exchange. Sodium hypochlorite followed by ammonium sulfate are then added to the carrier water using static mixers. The carrier water flow rate is set to target a 50x dilution to prevent heat buildup and chemicals are dosed for a 4.5:1 Cl_2:N ratio for optimal monochloramine formation. Monochloramine stock was collected daily during testing and fed using a peristaltic pump which was calibrated each time the chloramine addition point was changed. Monochloramine stock was kept on ice to prevent decay and used within four hours of collection. The stock concentration was measured each time it was collected and at the end of each testing day, never decaying more than 5%.

2.2. Analytical methods

Monochloramine, total chlorine, and free ammonia were measured using a Hach SL1000 Portable Parallel Analyzer (Hach, Loveland CO). Total ammonia, nitrite and nitrate were measured by TNT methods 830, 839, and 835, respectively, and quantified on a Hach DR 3900 spectrophotometer. Ozone residuals were measured by the gravimetric indigo method, Standard Methods 4500B-O_3, with malonic acid addition to mask and free chlorine from chloramination or any oxidized bromide species which may be present. Indigo absorbance at 600 nm as well as UV254 absorbance of the water samples were measured on a Genesys 180 UV–Vis spectrophotometer (Thermo Scientific, Waltham, MA).

Bromide and bromate were analyzed by ion chromatography via EPA methods 300 and 300.1, respectively. Bromate samples were preserved with EDA. In order to calculate total organic bromine, TOBr, ozone effluent bromide samples were also collected. The effluent bromide concentration was corrected for the bromide converted to bromate and compared to the influent after the method of Buffle et al. (2004). Ozone effluent bromide samples were quenched with 2 mM sodium bisulfite within one minute of sample collection.

NDMA and 1,4-dioxane were measured on an Agilent 7010B GC/MS Triple Quadrupole by EPA methods 521 and 522 with some slight modification. Notably, both samples were collected it the same 500 mL sample container preserved with 50 mg/L sodium sulfite and 1 g/L sodium bisulfate to dechlorinate and acidify the sample. Magnesium sulfate was used in place of sodium sulfate to dry the extract. Other slight deviations were as reported by Vaidya et al. (2021).

3. Results and discussion

3.1. Bromate formation

Without monochloramine addition, bromate formation increased from 0.3 to 39.9 μg/L by increasing the ozone dose from 0.31 to 1.18 O_3:TOC (3.75 to 9.6 mg/L applied O_3) as shown in Fig. 3. Bromide conversion to bromate of 2.9% at 0.86 O_3:TOC is in line with the bench testing results reported by Soltermann et al. (2016). With monochloramine addition immediately before ozonation, bromate formation was decreased by as much as 90% with 5 mg/L-Cl_2 NH_2Cl. A dose of 1 mg/L NH_2Cl reduced bromate formation by 68% on average, while 3 and 5 mg/L decreased it by 84% and 87%, respectively. Increasing monochloramine contact time to 8 min had no effect on bromate control and is discussed further below.

At the lowest ozone doses, targeting 0.3 O_3:TOC, there was no dose response observed (all bromate values were <1 μg/L) between monochloramine and bromate formed. In these tests, there was very little measured ozone residual in the effluent of the dissolution column. Other studies have shown very little BrO_3 formation at ozone doses below 0.4 O_3:TOC as there is very little ozone available to oxidize Br* and HOBr/OBr^- to form bromate (Soltermann et al., 2016).

As shown in Figs. 3and 4, there was minimal improvement in bromate by increasing monochloramine dose from 3 to 5 mg/L. Similar to both ammonia addition and the chlorine/ammonia based strategies, preformed monochloramine addition likely has a point of diminishing return where increasing dose has limited or no effect on controlling the bromate formation process (Buffle et al., 2004; Pinkernell and von

Table 2
Influent Water Quality Summary.

Parameter	pH	Temp	Alkalinity	TOC	Bromide	1,4-dioxane	NH_4	NO_2	NO_3
Unit		°C	mg/L-$CaCO_3$	mg/L	mg/L	μg/L	mg/L-N	mg/L-N	mg/L-N
Mean	7.14	20.0	178.3	6.60	0.422	0.52	0.36	0.122	2.27
Standard Deviation	0.05	0.8	7.51	0.31	0.020	0.04	0.22	0.145	0.46
Min	7.08	19.3	174	6.12	0.397	0.49	0.06	0.000	1.13
Max	7.23	22.4	184	6.9	0.457	0.56	0.519	0.498	2.80

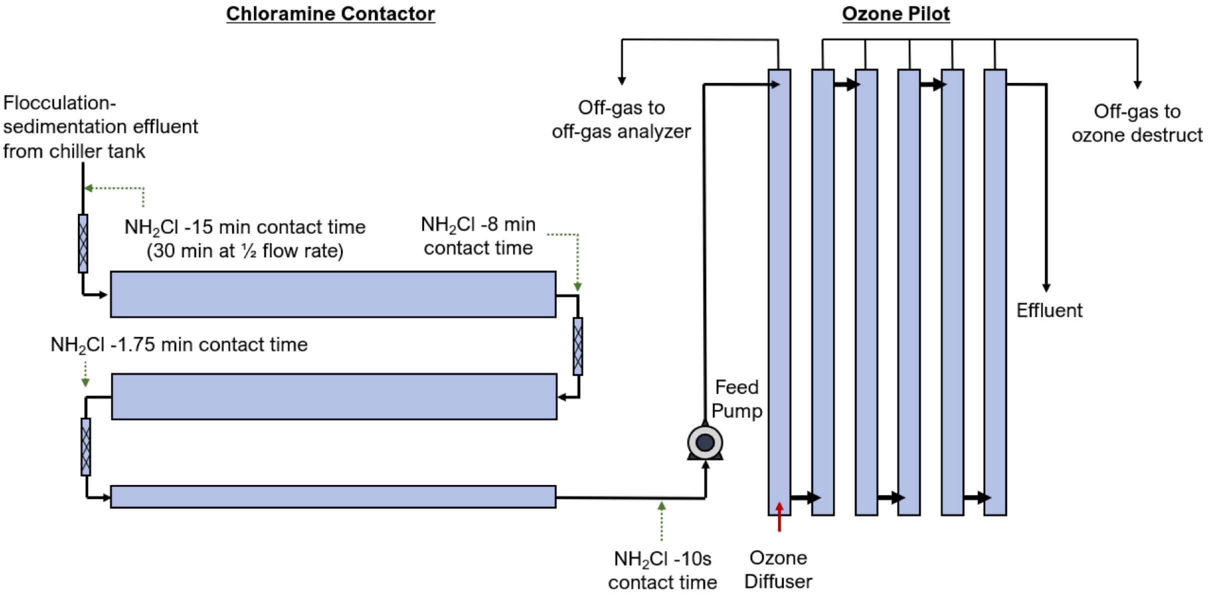

Fig. 2. Ozone pilot and chloramine contactor schematic.

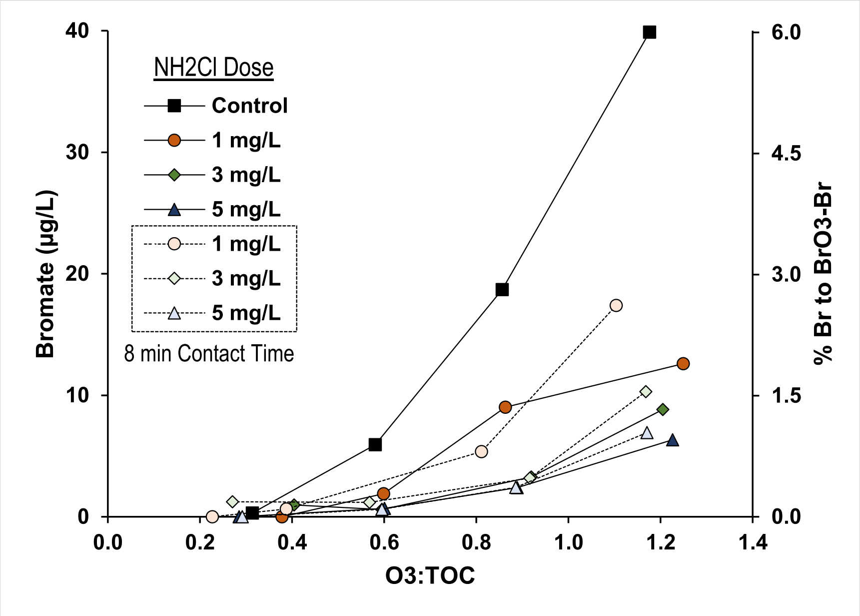

Fig. 3. Bromate formation with increasing ozone dose at various monochloramine doses added either immediately before ozonation (solid symbols) or with eight minutes of contact time (open symbols) before ozonation. Br: 414 µg/L, TOC: 6.9 mg/L.

Gunten, 2001). The location of this point is most likely water quality dependent. Benotti et al. (2011) saw no additional bromate suppression from increasing NH$_2$Cl from 1 mg/L to 2 mg/L, while Ikehata et al. (2013)observed a significant improvement. Interestingly, Ikehata et al. had 35% lower bromide but higher pH and TOC which may have increased their *OH generation and bromate formation for similar ozone doses. While some water quality parameters fluctuated over the course of testing, mainly NO$_2^-$, it is assumed that the nature and reactivity of DOM did not change.

3.2. *Monochloramine as a *OH scavenger*

1,4-dioxane removal decreased from 49% to 33% by increasing monochloramine dose from 0 to 5 mg/L at a fixed ozone dose of 7 mg/L (Fig. 4). This demonstrates that monochloramine is acting as a hydroxyl radical scavenger as 1,4-dioxane is ozone resistant and only removed by *OH (k_{O3}= <1 M^{-1}s^{-1}, k_{*OH} = 3(10^9) M^{-1}s^{-1}) (von Sonntag and von Gunten, 2012). This is particularly important for wastewater ozonation where more bromate is formed through the indirect *OH pathways (Soltermann et al., 2017).

1,4-dioxane samples were also collected with the control and 5 mg/L NH$_2$Cl in the test matrix shown in Fig. 3, and 1,4-dioxane removal decreased by roughly half (Fig. S1). A similar result was observed during ozonation at the 3.8 MLD scale by Hogard et al. (2021). Change in UV absorbance at 254 nm has been shown to be a good surrogate measure for *OH exposure and 1,4-dioxane removal (Gerrity et al., 2012; Wert et al., 2009). UV absorbance measurements were taken for all tests and were well correlated with 1,4-dioxane removal. These results show that *OH scavenging is occurring by monochloramine in all cases (Figs. S2–S4).

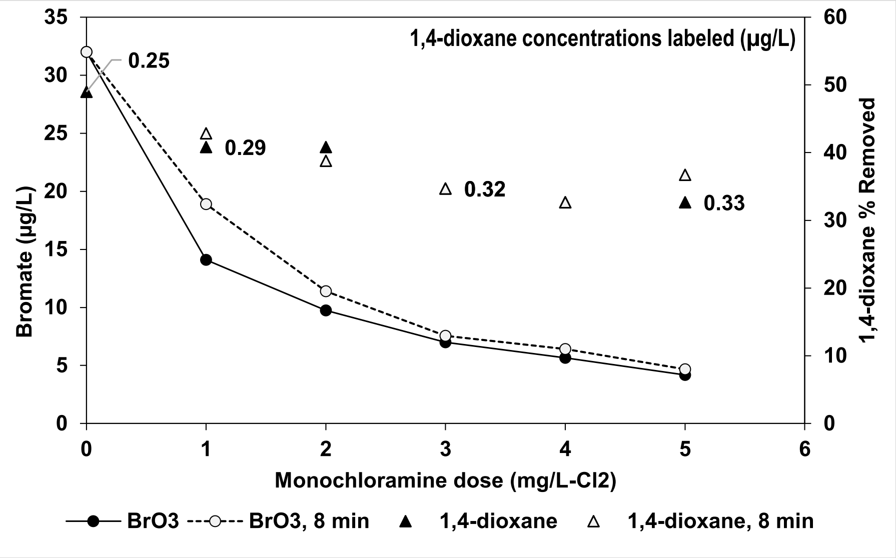

Fig. 4. Bromate formation and 1,4-dioxane removed with increasing monochloramine at a fixed ozone dose of 7 mg/L. 397 µg/L Bromide, 0.49 µg/L initial 1,4-dioxane.

Decreasing hydroxyl radical exposure by as much as 40 percent reduces bromate formation but it may also significantly reduce the oxidation capacity of the system. If non-biodegradable, ozone recalcitrant compounds such as 1,4-dioxane, atrazine, or meprobamate are an issue (or MIB and geosmin in drinking water), use of monochloramine for bromate suppression may be problematic. High ozone doses are often required to get sufficient removal of these compounds, in which case monochloramine use for bromate control is counterproductive. Some compounds with moderate reactivity with ozone, such as gemfibrozil and atenolol, are removed by both ozone and hydroxyl radicals (Lee et al., 2013). With monochloramine addition, ozone dose may need to be increased in order to account for the lower *OH exposure to remove these compounds. Additionally, increasing chloramine doses also increase the chemical dose required to quench monochloramine before biofiltration, and the addition of nitrogen with preformed monochloramine may require increased nitrogen removal in the wastewater treatment plant to meet total nitrogen or nitrate limits. On the other hand, many trace organic contaminants are oxidized quickly by molecular ozone at low ozone doses. Compounds such as diclofenac or sulfamethoxazole with $k_{O3} > 10^4\ \mathrm{M^{-1}s^{-1}}$ are primarily removed by ozone despite their high reactivity with *OH.

3.3. Monochloramine contact time

Increasing monochloramine contact time upstream of ozonation was tested to determine if bromochloramine formation (Table 1 Reaction 4) prior to ozonation further decreases bromate formation. Two conditions were tested including (1) monochloramine addition directly before the pilot feed pump, approximately 10 s before entering the ozone contactor, and (2) monochloramine addition eight minutes upstream using a small pipeline contactor for the tests shown in Figs. 3and 4. Eight minutes of chloramine contact prior to ozonation did not result in decreased bromate formation. Contact times up to 30 min were also tested (Fig. 5) and no decrease in bromate formation was observed.

Ling et al. (2020) showed ~92% masking of bromide as NHBrCl, $NHBr_2$, and NH_2Br with six minutes of NH_3—Cl_2 pretreatment and even greater with 10 min. This was said to be occurring through reactions with NH_2Cl suggesting preformed monochloramine should behave similarly. Ideally, masking of bromide prior to ozonation would improve bromate suppression allowing the chemical doses to be decreased. This

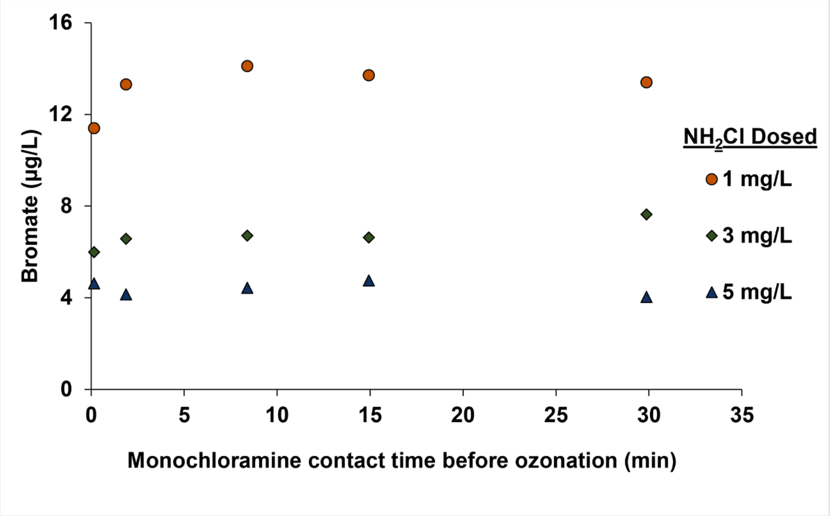

Fig. 5. Bromate formed as a function of monochloramine contact time prior to ozonation at a fixed ozone dose of 7 mg/L. Br: 413 µg/L.

would, in turn, decrease radical scavenging by NH_2Cl and improve 1, 4-dioxane removal. However, that was not the case for this study. Luh and Mariñas (2014) claimed that the Trofe et al. (1980) mechanism (Table 1 Reaction 4) was inaccurate and showed that it would take several hours for bromochloramine to form at NH_2Cl and Br^- concentrations relevant to water treatment. Ling et al. (2020) and Luh and Mariñas (2014) both use spectrophotometric methods in pure waters; however, they assume different absorbance peaks for NHBrCl measurement. Unfortunately, in real water samples with the background absorbance of the water matrix, these methods are not applicable. The DPD total chlorine and indophenol monochloramine methods used in this study cannot distinguish between the various haloamine species.

In either case, there does not appear to be any practical benefit of increasing monochloramine contact time for bromate control. In many of the tests (Figs. 3and 4), it appeared that the slight decay in NH_2Cl over the contact time resulted in decreased bromate suppression. At the SWIFT Research Center, preformed monochloramine is added to the ozone sidestream immediately before the venturi injector. This effectively doubles the monochloramine dose in the sidestream with a ~50/50 sidestream flow split and decreases bromate formation by several μg/L (data not shown). This arrangement would not be feasible with increased monochloramine contact time to the entire flow.

3.4. Intermediate masking

Fig. 4 shows a significant decrease in bromate formation with the addition of 1 mg/L NH_2Cl followed by a more gradual decrease with increasing dose thereafter. 1,4-dioxane removal shows a gradual decrease throughout. *OH radical exposure, calculated using 1,4-dioxane as a probe compound with $k_{*OH} = 3(10^9)\ M^{-1}s^{-1}$, was decreased by 22% at 1 mg/L NH_2Cl and 41% at 5 mg/L NH_2Cl while bromate was reduced by 56 and 87 percent, respectively. This suggests that *OH radical scavenging is not the only method of bromate suppression by monochloramine. While it does not appear that NHBrCl is forming prior to ozonation, it can be formed from HOBr and NH_2Cl during ozonation (Table 1 Reaction 2). Additionally, some free ammonia was always fed with the monochloramine stock solution to ensure only monochloramine was formed. Therefore, NH_2Br can also be formed during ozonation via Reaction 1 (Table 1). As HOBr only reacts with the nonionic form, NH_3, the effective rate constant between HOBr and total ammonia (NH_3 & NH_4^+) at pH 7 is similar to that of bromochloramine formation, so both compounds are likely to form as intermediates.

3.5. Ozone demand, decay, and disinfection credit

Fig. 6 shows ozone decay with increasing monochloramine dose with a 7 mg/L applied ozone dose. The first ozone residual measurement was excluded from the decay rate calculations as it does not fit the linearized 1st order ozone decay curves. This first point was taken at the outlet of the dissolution column, approximately 2.5 s after the ozone diffuser where the initial/instantaneous demand phase of ozone decay would not yet be complete. Increasing monochloramine dose had no effect on ozone decay rate. This shows that ozone decay and *OH generation is controlled by direct reactions with DOM rather than by radical chain reaction and not affected by the addition of a radical scavenger. In another study, and previous testing with this pilot at a different HRSD treatment plant, an increase in ozone decay rate was observed with monochloramine addition (Pearce et al., 2018; Benotti et al., 2011). This was hypothesized to be due to monochloramine oxidation to nitrate by ozone via Reaction 5 in Table 1. Some monochloramine decay was observed through ozonation (data not shown). Benotti et al. (2011) had to increase their ozone dose by approximately 15 percent to achieve the same *Cryptosporidium* CT credit in river water when adding 1 mg/L monochloramine. However, that does not appear to be the case in the present study. This indicates that slower reacting compounds with rate constants on the order of 26 $M^{-1}s^{-1}$ do not control ozone decay rate.

Overall, ozone decay rate decreased with increasing ozone dose and was unaffected by monochloramine addition as shown in Fig. 7a. Initial or instantaneous ozone demand (IOD) is operationally defined as the difference between the transferred ozone dose and the measured residual at the outlet of the dissolution column. IOD increased linearly with increasing dose but decreased as a fraction of the transferred dose (Fig. 7b). Even at the highest ozone dose, IOD was still greater than 50% of the transferred ozone dose. IOD was also unaffected by monochloramine addition as direct reactions with DOM control ozone decay during this phase and play a larger role in wastewater ozonation (Buffle et al., 2006). Table 3 shows the calculated virus and *Cryptosporidium* log-inactivation credits. For viruses, CT was calculated using the maximum of the single point CT from the measured ozone residual samples multiplied by the retention time from the outlet of the dissolution column to the respective sample port. In wastewater with high ozone decay rates, the measured single point CT can vary significantly for the same ozone residual profile depending on where the residual is measured. Even when optimized the single point CT method is extremely conservative and significantly underestimates the true ozone exposure in the system. Despite this, all but the lowest doses tested were sufficient for significant viral inactivation credit as shown in Table 3. One-log virus credit was given for dissolution column effluent ozone residuals >0.1 mg/L. For *Cryptosporidium* CT was calculated by integrating the first order ozone residual decay curves. This is approximately equivalent to the Extended CSTR or Extended T_{10} methods typically used to achieve *Cryptosporidium* CT credit (Rakness et al., 2005). A baffle

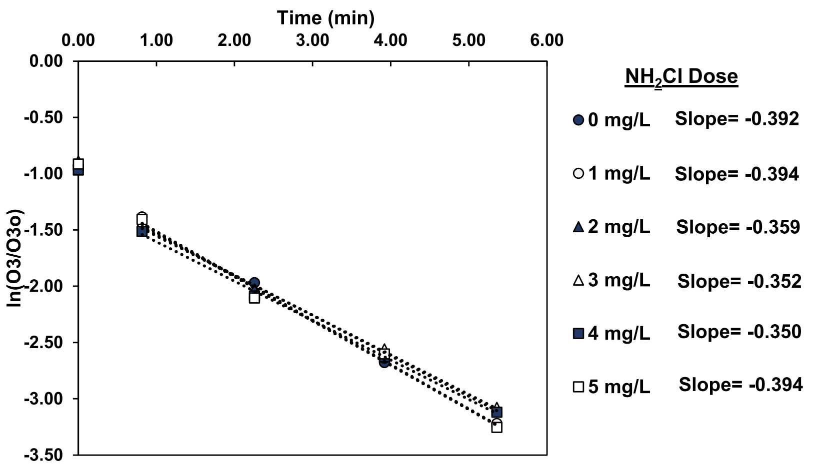

Fig. 6. Linearized first order ozone decay curves at a fixed ozone dose of 7 mg/L.

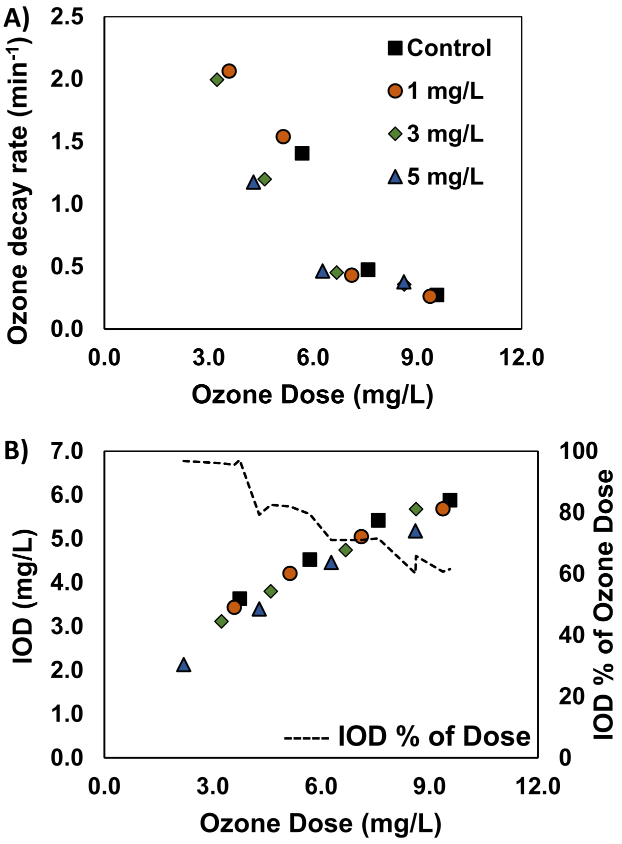

Fig. 7. A) ozone decay rate and B) initial ozone demand, IOD, vs. ozone dose at varying monochloramine doses.

factor of 0.9 was applied in all cases to approximate the pipeline contactor at the SRC.

The calculated log-inactivation credit from the chemical dose matrix decreases with increasing monochloramine dose. However, this is likely due to the ozone doses being increased during the control test for nitrite demand which decreased throughout the testing day while monochloramine doses were increased. With a fixed ozone dose of 7 mg/L (1.07 O_3:TOC), increasing monochloramine dose had no effect on the calculated *Cryptosporidium* LRV. HRSD currently operates the ozone system at the SWIFT Research Center to achieve 3-log virus inactivation credit using a single-point CT calculation in a pipeline contactor. From these pilot tests, this target would be achieved around 0.6 to 0.8 O_3:TOC which is consistent with full-scale operation (Hogard et al., 2021). Two-log *Cryptosporidium* inactivation credit would require an ozone dose of approximately 1:1 O_3:TOC (when using an integrated CT method). A dose of 3 mg/L-Cl_2 preformed monochloramine was able to keep bromate below the MCL at ozone doses as high as this. In terms of contaminant oxidation, ozone doses this high are mostly beneficial for the removal of more ozone recalcitrant compounds whose removal may be negatively affected by hydroxyl radical scavenging by monochloramine. Unless ozone CT is necessary for a secondary barrier to *Cryptosporidium*, it may be easier to achieve this removal elsewhere as many O_3-BAF based reuse treatment trains utilize membrane filtration or downstream UV disinfection (Gerrity et al., 2013).

3.6. NDMA and brominated organics

Fig. 8 shows the ozone effluent NDMA with and without monochloramine addition. These samples were taken during the control and 5 mg/L NH_2Cl conditions shown in Figs. 3 and S1. NDMA formation increased with increasing ozone dose until it plateaued around 0.6 O_3:TOC which is consistent with previous results on this water and other literature results (Hogard et al., 2021; Snyder et al., 2015).

Monochloramine addition did not increase NDMA formation. While both monochloramine and ozone can form NDMA, they are formed by distinctly different groups of precursors (Sgroi et al., 2018). Many NH_2Cl-NDMA precursors are well removed by ozonation (Lee et al., 2007). NDMA formation potential tests conducted on this water by Vaidya et al. (2021) showed an average of 780 ng/L NDMA formed with 140 mg/L-Cl_2 NH_2Cl after 10 days of contact. An ozone dose of 0.6 O_3:TOC decreased formation potential by approximately 90%. In previous testing by Hogard et al. (2021), increased ozone effluent NDMA was observed at 2 mg/L O_3 with 3 mg/L preformed monochloramine. This indicated that 2 mg/L ozone was insufficient to remove the NH_2Cl-NDMA precursors and that monochloramine could form NDMA in the eight-minute contact time of the ozone contactor. However, that did not appear to be the case here.

A dose of 5 mg/L-Cl_2 preformed monochloramine was added to the settled water and NDMA was sampled over 90 min (Table S1). No NDMA formation was observed, which is not unexpected as NDMA formation by monochloramine is typically quite slow, on the order of days in drinking water distribution systems. Preforming monochloramine should also minimize the risk of NDMA formation by dichloramine (Schreiber & Mitch, 2006). Even at the lowest ozone doses, NDMA was greater than most drinking water regulatory limits of 10 ng/L, indicating that removal by downstream biofiltration or UV photolysis would be required.

The formation of brominated organic disinfection byproducts is also a concern with chlorination and chloramination of bromide containing waters. Though most of these compounds are unregulated, they are thought to be more toxic than their chlorinated counterparts (Sharma et al., 2014). Buffle et al. (2004) showed significant total organic bromine (TOBr) formed during the Cl_2—NH_3 process. As much as 30% of the of the initial bromide ended up as TOBr, and this was reduced to approximately 15% with increased background ammonia causing NH_2Cl formation.

In this study, effluent bromide was measured on select samples with ozonation and chloramination (Table S2). TOBr, estimated as "missing" bromide between the ozone influent and effluent and corrected for bromate, was always less than 5% which is well within the range of analytical error and influent bromide fluctuation. Brominated organic formation does not appear to be a concern here. Similar to NDMA formation, it may take more time for these compounds to form. Ozonated samples were quenched with bisulfite within one minute of sample

Table 3
Calculated virus and *Cryptosporidium* log-reduction values.

Test LRV	Chemical Dose Matrix Virus LRV				*Cryptosporidium LRV*				NH_2Cl Dose Curve *Crypto LRV*
O_3:TOC	0.3	0.6	0.9	1.2	0.3	0.6	0.9	1.2	1.07
0 mg/L NH_2Cl	1.1	3.3	13.1	40.5	0.02	0.35	2.1	5.6	2.9
1 mg/L NH_2Cl	1.1	2.6	11.1	32.4	0.02	0.27	2.0	5.5	3.0
2 mg/L NH_2Cl									3.2
3 mg/L NH_2Cl	1.1	2.1	9.6	23.8	0.01	0.24	1.7	3.7	3.1
4 mg/L NH_2Cl									2.9
5 mg/L NH_2Cl	1.0	2.3	9.2	23.0	0.01	0.27	1.6	3.8	3.0

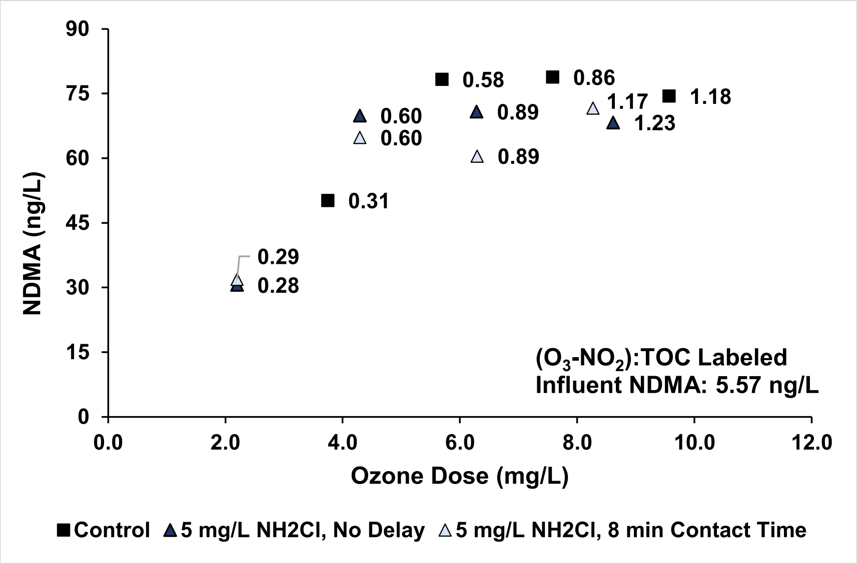

Fig. 8. Ozone effluent NDMA vs. ozone dose with and without preformed monochloramine addition.

collection giving a maximum contact time of 8 min with monochloramine plus 10 min through the ozone contactor and sample collection. Bromide samples were also collected with NDMA with up to 90 min of monochloramine contact time (Table S1) and again, no brominated organic formation was observed, at least within the sensitivity of the difference in the bromate-corrected bromide concentrations.

4. Conclusions

- With a bromide concentration of 414 μg/L, bromate exceeded the MCL of 10 μg/L at specific ozone doses greater than ~0.7 O_3:TOC. Monochloramine doses of 3 or 5 mg/L-Cl_2 NH_2Cl were able to control bromate formation to below the MCL at ozone doses up to 1.2:1 O_3:TOC and suppress bromate formation by as much as 90%. There was little improvement by increasing the monochloramine dose from 3 to 5 mg/L-Cl_2.
- Monochloramine is acting as a hydroxyl radical scavenger as evidenced by diminished 1,4-dioxane removal with increasing monochloramine dose. Use of monochloramine is a tradeoff between radical scavenging for bromate control and decreased removal of ozone resistant compounds which are removed through *OH oxidation alone. Removal of the most ozone reactive trace contaminants should be unaffected. Use of monochloramine for bromate control should come with serious evaluation of oxidation objectives.
- Increasing monochloramine contact time upstream of ozonation did not improve bromate control, indicating that bromide is not being masked as haloamines prior to ozonation. Monochloramine should be added as soon before ozonation as possible as monochloramine decay over longer contact times appeared to decrease bromate suppression.
- Monochloramine addition did not have any effect on ozone demand, decay rate, or calculated disinfection credit which is counter to previous drinking water results. This shows that ozone decay is unaffected by a radical terminator and that slow reactions between ozone and compounds such as monochloramine do not play much of a role in wastewater effluent. Though this may be water quality dependent.
- NDMA formation increased with increasing ozone dose until ~0.6 O_3:TOC where it plateaued at 60–75 ng/L. NDMA formation through ozonation was not affected by monochloramine addition for bromate control. It is likely that the short contact time before ozonation is insufficient for NDMA formation by monochloramine. However, the precursors may not have been present during these tests as precursor concentrations can be dependent on the source water and upstream treatment plant operation.
- Brominated organic formation does not appear to be a concern through ozonation either with or without monochloramine addition as there was a near perfect mass balance on bromide when accounting for bromide converted to bromate.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.118049.

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