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## Multi-point ozone dissolution for enhanced bromate control with hydrogen peroxide in potable reuse

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In the present study, a novel pilot ozone contactor configuration was employed using hydrogen peroxide ( $H_2O_2$ ) and multiple ozone diffusion zones in an over-under contactor for testing three wastewater effluents. With a 1:1 molar  $H_2O_2$ : $O_3$  dose, splitting the ozone dose between three diffusers reduced bromate formation by as much as 93% compared to the traditional single diffuser control condition. The required  $H_2O_2$  dose for similar bromate levels was decreased by more than 90%. 1,4-Dioxane was used as a representative contaminant and hydroxyl radical ( $\cdot OH$ ) probe compound.  $H_2O_2$  addition significantly improved 1,4-dioxane removal, and removal was similar between different diffuser conditions for the same total ozone dose. Detailed ozone residual and ozone exposure measurements showed that, with  $H_2O_2$ , similar ozone exposure was provided between the single and multi-diffuser  $H_2O_2$  experiments. This indicates that minimization of local ozone concentration, rather than exposure, is vital for preventing the  $O_3$ -Br<sup>-</sup> reaction which controls bromate formation and may be beneficial for removal of ozone reactive contaminants and disinfection. Ozone decay, both with and without  $H_2O_2$ , was extremely sensitive to pH. Bromate formation increased by a factor of nearly two from pH 6 to 8 in the control condition, while the effect was less pronounced with  $H_2O_2$ . 1,4-Dioxane removal was unaffected by pH or temperature, while bromate formation decreased with increasing temperature.

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### Water impact

Our study showed that using an ozone contactor with multiple diffusion zones could significantly reduce bromate formation in ozonation with hydrogen peroxide. High levels of 1,4-dioxane removal could be achieved with lower hydrogen peroxide doses required when compared to a single ozone addition point. This approach makes hydrogen peroxide a viable option for bromate control in wastewater ozonation.

## 1. Introduction

Removal of trace organic contaminants from wastewater is an important consideration for the implementation of potable reuse. Many contaminants of emerging concern or CECs are not well removed through wastewater treatment processes and pose potential environmental and human health risks such as carcinogenicity and endocrine disruption.<sup>1</sup> In the 'carbon-based' water reuse treatment approach, consisting of ozone ( $O_3$ ), biologically active carbon filtration (BAC), and granular activated carbon adsorption (GAC), ozonation serves as the first barrier against these compounds.<sup>2-4</sup> Ozone itself is a powerful selective oxidant which also generates hydroxyl radicals ( $\cdot OH$ ) through its

decomposition and reactions with organics when applied to wastewater. Thus, wastewater ozonation is inherently an advanced oxidation process (AOP).<sup>5</sup>

Ozone can directly oxidize many CECs such as carbamazepine, bisphenol-A (BPA), and sulfamethoxazole at low doses due to their high reactivity with ozone ( $k_{O_3} > 10^5 M^{-1} s^{-1}$ ). Other compounds which are more resistant to ozone are either partially ( $10 < k_{O_3} < 10^5 M^{-1} s^{-1}$ ) or entirely degraded by  $\cdot OH$  ( $k_{O_3} < 10 M^{-1} s^{-1}$ ,  $k_{\cdot OH} > 10^9 M^{-1} s^{-1}$ ).<sup>6,7</sup> One such compound is 1,4-dioxane which frequently occurs in wastewater due to industrial contamination and from household cleaning and cosmetic products, where it is an impurity formed from the production of ethoxylated surfactants.<sup>8,9</sup> It is a known human carcinogen with a  $10^{-6}$  lifetime cancer risk associated with a concentration of  $0.35 \mu g L^{-1}$ .<sup>10</sup> While it is not regulated on the federal level, several US states have set maximum contaminant levels.<sup>11</sup> In California,  $0.5 \log$  (69%) removal must be demonstrated for reuse AOP applications.<sup>12</sup> A recent review found the median

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concentration reported in wastewater to be  $0.72 \mu\text{g L}^{-1}$ .<sup>13</sup> Due to its prevalent occurrence and well-established rate constant with hydroxyl radicals ( $k_{\cdot\text{OH}} = 3.1(10^9) \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\cdot\text{O}_3} = 0.32 \text{ M}^{-1} \text{ s}^{-1}$ ), it is often used for the validation of UVAOP reactors and can be used as a hydroxyl radical probe compound to estimate the removal of other ozone resistant contaminants.<sup>14</sup> Additionally, unlike most other ozone resistant compounds, 1,4-dioxane is not adsorbed, photolyzed, or readily biodegraded, making its removal through ozonation critical for carbon-based reuse applications without UVAOP downstream.<sup>15</sup>

To maximize hydroxyl radical exposure for the degradation of 1,4-dioxane, higher ozone doses are necessary. Gerry and Wert<sup>16</sup> found that ozone doses of 1.0 to 1.5 mg O<sub>3</sub>:mg TOC were required for 0.5 log removal in bench testing of wastewater effluents. However, bromate formation may become problematic at ozone doses greater than 0.5 O<sub>3</sub>:TOC when bromide is present.<sup>7,17,18</sup> Bromate is a potentially carcinogenic disinfection byproduct formed through ozonation with a USEPA and EU drinking water maximum contaminant level (MCL) of  $10 \mu\text{g L}^{-1}$ .<sup>19</sup> Bromate is formed through a complex series of both ozone and hydroxyl radical reactions with bromide. In wastewater, most bromate is formed through the *indirect* pathway which is driven by the reaction between hydroxyl radicals and bromide, highlighted in Fig. 1.<sup>19,20</sup> Several chemical bromate control strategies developed in drinking water have been applied for bromate control in wastewater reuse. Notably, monochloramine can significantly reduce bromate formation during ozonation by scavenging hydroxyl and bromine (Br·) radicals and forming intermediate products which prevent bromate formation.<sup>7,19,21</sup> However, hydroxyl radical scavenging decreases the removal of ozone resistant compounds such as 1,4-dioxane, primidone, iohexol, meprobamate, and DEET.<sup>21–23</sup>

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can be used to enhance the conversion of ozone to hydroxyl radical. Bromate formation is suppressed by limiting ozone concentration and exposure due to the increased ozone decay rate and reducing hypobromous acid (HOBr) as shown in Fig. 1. The effectiveness of H<sub>2</sub>O<sub>2</sub> for bromate control reported in

literature is highly variable when using traditional dosing and dissolution techniques. In both drinking water and wastewater applications, H<sub>2</sub>O<sub>2</sub> has been reported to either increase or suppress bromate formation.<sup>18,24</sup> Detailed O<sub>3</sub> and ·OH kinetic measurements are not always reported, making it difficult to determine the exact mechanisms at play.<sup>19</sup> When effective, 30–60% bromate suppression is typical for a 1:1 mol H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> ( $0.71 \text{ mg mg}^{-1}$ ) dose, though higher doses may be used to further decrease bromate formation.<sup>18,19,22</sup> A review of bench and pilot scale data found that the H<sub>2</sub>O<sub>2</sub> dose required to achieve comparable levels of bromate suppression to monochloramine in wastewater ozonation would be cost prohibitive for full scale implementation.<sup>23</sup>

With limited ozone exposure and sufficient H<sub>2</sub>O<sub>2</sub> to quench HOBr that is formed, the reaction between Br· and O<sub>3</sub> becomes the critical bromate formation reaction.<sup>20</sup> As Br· also reacts quickly with bromide and dissolved organic matter (DOM), the ozone concentration then controls whether Br· is oxidized to form BrO·.<sup>26,28</sup> Ozone contactor and dissolution design can therefore be optimized for oxidation with bromate control by delivering multiple smaller ozone doses.<sup>29</sup> There are several commercial systems that operate on this premise, though this is not always clearly stated.<sup>30–32</sup> The MEMBrO<sub>3</sub>X concept operates by passing water through a hollow fiber membrane surrounded by ozone gas which then diffuses into the water. This was shown to be extremely effective for removing the ·OH probe compound *para*-chlorobenzoic acid (pcBA) while minimizing bromate formation in groundwater and surface water.<sup>33</sup> However, the applicability of these systems for large treatment plants is limited, and there has been little study on their use for wastewater reuse.

In the present study, a pilot scale ozone contactor was configured to allow ozone dosing with up to four diffusion zones, representing multiple diffuser grids in a traditional over-under baffled contactor (Fig. 2). Tests were conducted on multiple wastewaters in order to characterize the performance of ozone–peroxide with multi-point ozone dissolution and to inform full-scale design and operation. The objectives of this study were to (1) evaluate the efficacy of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> with multi-point dissolution for bromate control

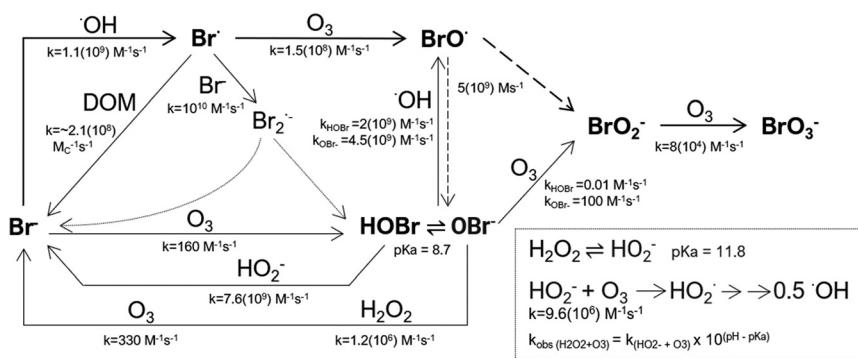


Fig. 1 Bromate formation pathways and mechanisms of mitigation by hydrogen peroxide. Closely adapted from Buffle *et al.*,<sup>25</sup> with reactions and rate constants from Lei *et al.*,<sup>26</sup> and von Sonntag and von Gunten.<sup>27</sup>



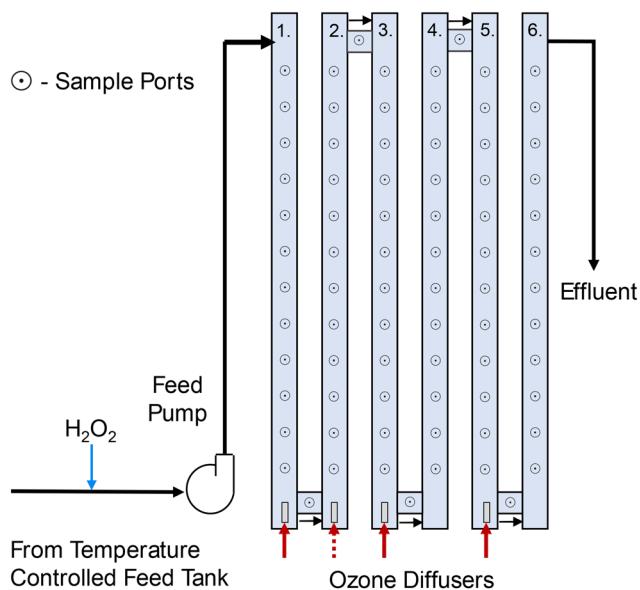


Fig. 2 Pilot ozone contactor diagram.

while maximizing the degradation of 1,4-dioxane, (2) determine the required chemical doses for bromate control, (3) examine the effects of water quality on bromate formation and control.

## 2. Materials and methods

### 2.1 Project background and sample collection

Hampton Roads Sanitation District's (HRSD) Sustainable Water Initiative for Tomorrow (SWIFT) is planning to add  $O_3$ -BAC-GAC based treatment to meet drinking water standards for managed aquifer recharge at up to five full-scale treatment plants. Treated effluent from three of these treatment plants was used for this study.

Plant A, York River Treatment Plant (Seaford, VA), is a nitrifying activated sludge plant with tertiary deep bed denitrification filters. The plant utilizes step feed and intermittent aeration with ammonia vs.  $NO_x$  (AvN) control followed by partial denitrification-anammox for nitrogen removal in the denitrification filters as described elsewhere.<sup>34</sup> Denitrification filter effluent was collected for testing. Bromide concentrations are typically 0.3 to 0.4 mg L<sup>-1</sup> due to saltwater infiltration into the collection system.

Plant B, Nansemond Treatment Plant (NTP), is a 5-stage Bardenpho plant located in Suffolk, VA. NTP receives roughly 15% of its influent from industry and a portion of the TOC in the secondary effluent is thought to be recalcitrant organic matter from these industrial sources. Bromide was primarily from landfill leachate as well as saltwater infiltration, 0.30 mg L<sup>-1</sup> average. Bromide will likely increase up to approximately 0.6 mg L<sup>-1</sup> in the future with increased flows from an additional collection system.

Plant C, Virginia Initiative Plant (Norfolk, VA) uses a 5-stage VIP +2 process for nutrient removal. The high level of bromide is from saltwater intrusion (0.6–1.1 mg L<sup>-1</sup> tested,

1.5 mg L<sup>-1</sup> average). Plant C also receives flows from a centralized waste treatment facility which results in intermittently high levels of 1,4-dioxane.

Tests were conducted on a pilot plant operated at Nansemond Treatment Plant (plant B). Effluent water from plants A and C (tertiary and secondary, respectively) was collected upstream of disinfection in a 15 m<sup>3</sup> tanker truck and transported to plant B. The pilot was configured to run directly on plant B secondary effluent, from the tanker truck used to collect water from plants A and C, or held in an 80 m<sup>3</sup> storage tank which allowed 1,4-dioxane and bromide to be spiked for select tests. Temperature was controlled in a 0.6 m<sup>3</sup> pilot influent feed tank using an aquarium chiller or immersion heater depending on the desired temperature.

### 2.2 Pilot treatment system

The pilot system used for the ozonation tests was a modified Intuitech second generation ozone pilot (Intuitech Inc., Salt Lake City, USA). The pilot was operated at 4.0 L min<sup>-1</sup> and had an ozone contactor consisting of six 5 × 290 cm contact columns in series with a detention time of 1.5 minutes each. Each column had a series of 12 sample ports as well as sample ports between the columns which allowed for the collection of detailed ozone residual profiles and other sampling throughout the contactor. Ozone was added using fritted 316 stainless steel diffusers in the bottoms of the dissolution columns. For the tests with up to three diffusers, ozone was added in the first, third, and fifth column for counter-current dissolution. A fourth diffuser was added to the second column (co-current) for select tests or where specified otherwise. A diagram of the pilot ozone contactor is shown in Fig. 2. For tests with six and eight diffusers, the pilot was operated with three or four diffusers, respectively, and the pilot effluent filled a 200 L HDPE drum which was then recycled to the influent for a second pass.

Two identical ozone generators were used in the tests with more than one diffuser, where each supplied ozone to two of the diffusers. Ozone was generated from oxygen from the onboard oxygen concentrator. Gas flow to each diffuser was controlled by two parallel mass flow controllers (MFCs) with a third gas stream going to the feed gas analyzer to determine the ozone gas concentration and resulting applied dose. The two generators together were configured to be able to run the four mass flow controllers and two feed gas analyzers in series to verify their accuracy each day of testing. Gas flow was held constant while the ozone generator varied the ozone concentration in order to meet the desired applied ozone dose. For the single diffuser tests, ozone concentrations ranged from 8 to 14% W/W. With multiple diffusers, ozone concentrations were as low as 3% in order to keep enough gas flow through the MFCs for them to control consistently at low flow rates. Due to the low gas flow rates used, 0.15–0.35 standard L min<sup>-1</sup> (SLPM), transfer efficiency could not be measured reliably. Ozone doses here refer to the applied dose through transfer efficiency was expected to be



>95% from previous pilot experiments at higher gas and water flow rates.

Ozone doses were determined each day of testing by collecting a grab sample for TOC and nitrite ( $\text{NO}_2^-$ ) and calculating the dose for the desired  $\text{NO}_2^-$  corrected  $\text{O}_3$ :TOC ratio or  $(\text{O}_3-\text{NO}_2^-)$ :TOC by eqn (1).

$$\text{Applied O}_3 \text{ dose (mg L}^{-1}\text{)} = \text{O}_3 : \text{TOC} \times \text{TOC} + \frac{3.43 \text{ mg L}^{-1} \text{ O}_3}{\text{mg L}^{-1}\text{-N NO}_2^-} \quad (1)$$

$\text{H}_2\text{O}_2$  dose was then determined for the proper molar  $\text{H}_2\text{O}_2 : \text{O}_3$  ratio. All  $\text{O}_3$ :TOC ratios used here are mass based and  $\text{NO}_2^-$  corrected (3.43 mg  $\text{O}_3$  per mg N) whereas hydrogen peroxide–ozone ratios are referred to in molar units. For the multi-diffuser tests, ozone doses were split evenly between the diffusers except where noted.

### 2.3 Testing plan

Water from each of the three plants was collected and first run through a matrix of ozone doses and diffuser configurations. During this test hydrogen peroxide was dosed at a fixed 1:1 molar ratio to the total ozone dose. In the following test, hydrogen peroxide dose was varied at a fixed ozone dose for all three plants. Detailed ozone residual and exposure profiles were measured with most tests to assess the mechanistic implications of multi-point dissolution on bromate formation, hydroxyl radical formation, and 1,4-dioxane removal. Following these experiments, water was collected periodically to evaluate the effects of common water quality parameters that varied between the plants and seasonally. These included: pH, temperature, ammonium, nitrite, TOC, and bromide.

To test the effects of TOC, plant B secondary effluent was run through a coagulation, flocculation, and sedimentation pilot. Aluminum chlorohydrate (ACH) was selected as a prehydrolyzed coagulant which did not change pH or alkalinity. An ACH dose of  $17.5 \text{ mg L}^{-1}$  as product decreased TOC by 34%. UV absorbance scans from 220 to 500 nm of coagulated water and secondary effluent diluted 30% with DI water were virtually identical, indicating ACH removed organic matter uniformly.

### 2.4 Chemical addition

Hydrogen peroxide stock was made by diluting reagent grade 30% unstabilized  $\text{H}_2\text{O}_2$  (Thermo Scientific or Lab Alley) to 0.3% in deionized water and fed into the pilot influent using a peristaltic pump immediately before the pilot feed pump to ensure good mixing. 1 to  $2 \mu\text{g L}^{-1}$  1,4-dioxane was spiked in the storage tank from a concentrated stock solution. Sulfuric acid, sodium hydroxide, sodium bromide, and sodium nitrite were added to the pilot influent or water storage tank for select tests.

### 2.5 Analytical methods

Ozone residuals were measured by the gravimetric indigo method (Standard Methods 4500-O<sub>3</sub>).  $\text{H}_2\text{O}_2$  was measured using the ferric thiocyanate method with a CHEMetrics I-2016 Peroxide SAM colorimeter (CHEMetrics, Midland, VA). The accuracy of these tests is roughly  $\pm 10\%$  and  $\text{NO}_2^-$  was found to interfere (Fig. S1). These measurements served more to verify chemical feed and to examine relative  $\text{H}_2\text{O}_2$  degradation through ozonation. Influent temperature was measured using a Hanna Instruments handheld thermometer. For most tests pH was analyzed by an Orion Starr A211 laboratory pH probe approximately hourly. pH was measured with every influent sample when pH was being controlled.

UV absorbance (254 nm) was measured on a Genesys 180 UV-vis spectrophotometer (Thermo Scientific, Waltham, MA). TOC was analyzed on a Shimadzu TOC 4200. Ammonia was measured by Hach TNT method 830 or 831, nitrite by TNT 831, and nitrate by TNT 835 on a Hach DR 3900 spectrophotometer. Alkalinity was measured in the field using a Hach SL1000 portable parallel analyzer *via* Hach method 10280 or by EPA 310.2.

Bromide and bromate were measured by ion chromatography using EPA methods 300 and 302, respectively. 1,4-Dioxane was analyzed by Eurofins Eaton Analytical by EPA method 522 or analyzed using a slightly modified version of EPA 522 (described elsewhere<sup>21</sup>).

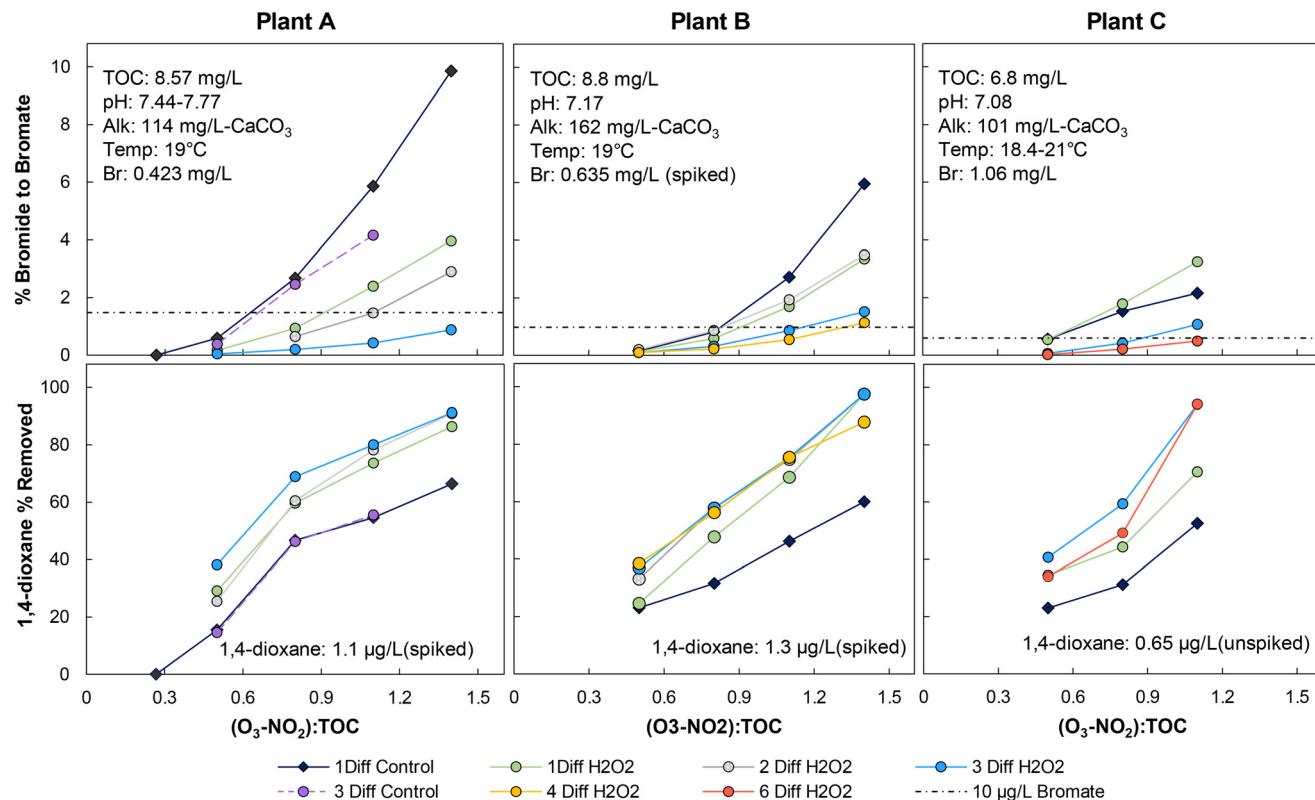
## 3. Results and discussion

### 3.1 Bromate formation and 1,4-dioxane removal

Bromate formation and 1,4-dioxane removal were examined over a range of ozone doses and diffuser configurations with hydrogen peroxide addition as shown in Fig. 3. In the single diffuser control condition, for a given  $\text{O}_3$ :TOC, bromate yield was highest at plant A, which may be due to the higher pH, discussed below, while it was lowest at plant C which had the highest bromide. With a single diffuser, the addition of  $\text{H}_2\text{O}_2$  at a 1:1 molar ratio to ozone (0.71 mg:mg), reduced bromate formation by 59 to 72% for plant A, 11 to 44% for plant B while for plant C bromate was only 2.2% lower at the lowest ozone dose and increased to 51% greater than the control at the highest ozone and  $\text{H}_2\text{O}_2$  dose.

On average, 1,4-dioxane removal increased by 26 percentage points with hydrogen peroxide addition. This indicates that hydroxyl radical exposure was significantly enhanced by peroxide addition and was similar between the different diffuser configurations. On the other hand, bromate formation was significantly reduced by splitting the ozone dose between increasing number of dissolution zones. This implies that multi-point dissolution does not necessarily enhance hydroxyl radical exposure, however, it does allow higher ozone doses to be applied while controlling bromate formation. The slight increase in bromate formation with two diffusers and  $\text{H}_2\text{O}_2$  for plant B was unexpected and cannot be explained by the





**Fig. 3** Bromate formed as molar conversion of bromide to bromate-Br and corresponding 1,4-dioxane removed with increasing number of ozone diffusers over a range of ozone doses. Hydrogen peroxide was dosed at a 1:1 molar ratio to the total ozone dose. 0.035 µg L<sup>-1</sup> was used to calculate 1,4-dioxane removal when effluent was < MRL (0.07 µg L<sup>-1</sup>).

measured ozone residuals and was not replicated in preliminary (data not shown) or subsequent tests (Fig. 8). For plant A, where bromate formation with three diffusers was already exceptionally low, four or more would likely be unnecessary. However, for plants B and C, increasing from three to four or six diffusers, respectively, decreased bromate formation further.

### 3.2 Hydrogen peroxide dosing

Fig. 4 shows that with a single diffuser, bromate decreased with increasing H<sub>2</sub>O<sub>2</sub> for plants A and B while it increased before decreasing again in plant C effluent. A dose of 4.0–4.5 H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> resulted in 29–84% reduction in bromate formation. This is consistent with previous results and the conclusion that, with a single ozone addition point in a traditional ozone contactor or bench test, excessive H<sub>2</sub>O<sub>2</sub> doses would be required to control bromate formation.<sup>23,35</sup>

Using three diffusers without H<sub>2</sub>O<sub>2</sub> decreased bromate formation by 45% for plant B, and 57% for plant C. Addition of 0.25 H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> decreased bromate formation by a further 41% for plant B but only 7% for plant C, bromate then continued to decrease with increasing H<sub>2</sub>O<sub>2</sub> dose. H<sub>2</sub>O<sub>2</sub> doses < 0.5 H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> were not tested for plant A, however, similar to plant B, the majority of bromate suppression was achieved with the lowest H<sub>2</sub>O<sub>2</sub> dose. For plants A and B, this

represents a chemical savings of upwards of 90% when compared to a single ozone addition point. Four and six diffusers were also tested for plants B and C, respectively. In this case, using four diffusers only marginally decreased bromate in plant B effluent while six diffusers did have a significant effect on plant C. Further increasing the number of diffusers may be helpful at higher bromide concentrations and is discussed further below.

1,4-Dioxane removal improved with increasing H<sub>2</sub>O<sub>2</sub> dose in all cases. Hydroxyl radical formation and exposure is often claimed to be maximized at 0.5 mol H<sub>2</sub>O<sub>2</sub>:mol O<sub>3</sub> based on the simplified stoichiometry of  $2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2\cdot\text{OH}$  in drinking water treatment.<sup>36,37</sup> However, in wastewaters with higher competing ozone demand, by compounds which may consume O<sub>3</sub> but not produce ·OH, it is hypothesized that increasing the H<sub>2</sub>O<sub>2</sub> dose may allow more O<sub>3</sub> to react with HO<sub>2</sub><sup>-</sup> to form ·OH. Hübner *et al.*<sup>35</sup> saw decreased hydroxyl radical exposure when H<sub>2</sub>O<sub>2</sub> was increased from 0.5 to 1.0 H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> in secondary effluent. This was thought to be due to ·OH scavenging by H<sub>2</sub>O<sub>2</sub> ( $k_{\text{H}_2\text{O}_2\cdot\text{OH}} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) which is commonly reported in drinking water.<sup>38,39</sup> However,<sup>40</sup> reported ·OH scavenging rates of  $2.72\text{--}9.52(10^5) \text{ s}^{-1}$  for various wastewater effluents, while 10 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> would only scavenge ·OH at a rate of  $7.9(10^3) \text{ s}^{-1}$ .

With H<sub>2</sub>O<sub>2</sub> addition to the pilot influent and ozone divided equally between the different diffusers, the effective

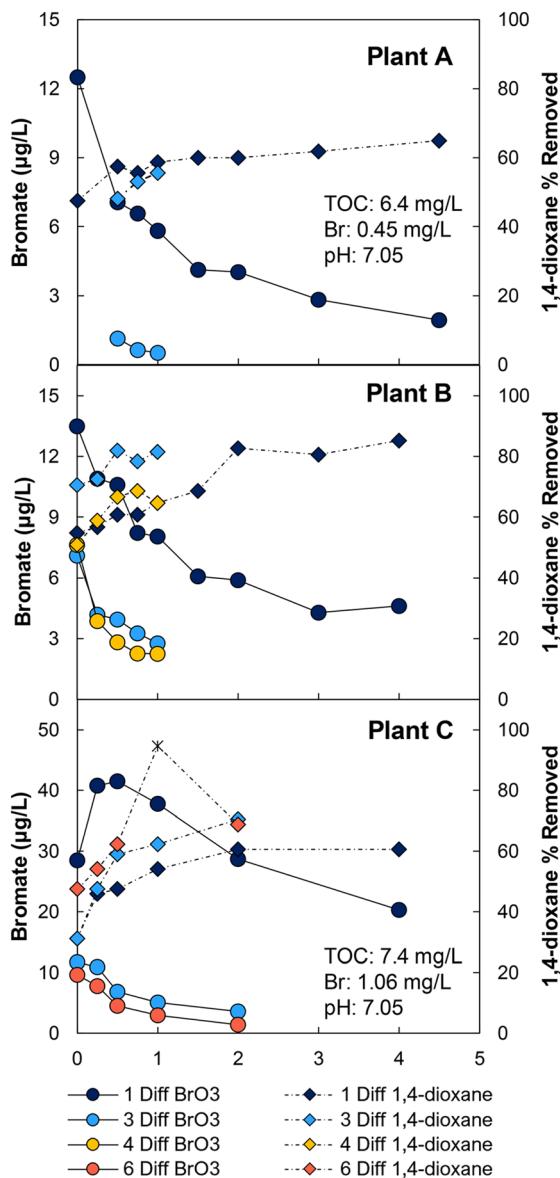


Fig. 4 Bromate formed and 1,4-dioxane removed at a fixed ozone dose of 0.8 ( $\text{O}_3\text{-NO}_2$ ):TOC. Temp: 19–21 °C. Lines added for visual aid. The asterisk symbol represents removal calculated using  $\frac{1}{2}$  the MRL for a value below detection.

$\text{H}_2\text{O}_2:\text{O}_3$  ratio at the first diffuser was three times the  $\text{H}_2\text{O}_2:\text{O}_3$  with respect to the total ozone dose when using three diffusers.  $\text{H}_2\text{O}_2$  was consumed slightly between the diffusers with the greatest decrease occurring in the final diffusion zone. This is consistent with a decrease in ozone demand and increase in ozone residual available to react with peroxide. For a 1:1  $\text{H}_2\text{O}_2:\text{O}_3$  dose,  $\text{H}_2\text{O}_2$  consumption was 20% on average for both the single diffuser and multi-diffuser configurations.  $\text{H}_2\text{O}_2$  consumption increased slightly with increasing ozone and  $\text{H}_2\text{O}_2$  dose when dosed at a constant oxidant ratio. At higher  $\text{H}_2\text{O}_2$  to ozone ratios,  $\text{H}_2\text{O}_2$  consumption increased on a concentration basis but decreased as a percentage of overall dose.

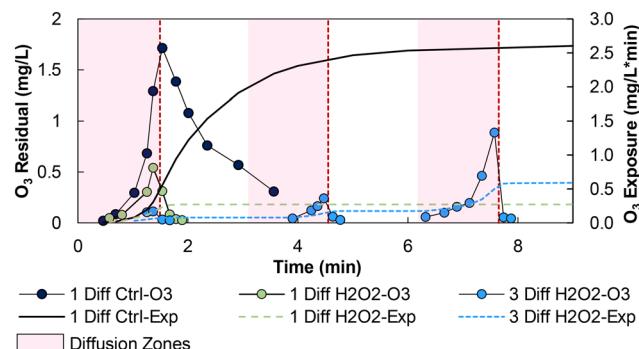


Fig. 5 Example ozone residual ( $-\text{O}_3$ ) and exposure ( $-\text{Exp}$ ) profile for plant A effluent at 0.8  $\text{O}_3$ :TOC (7.0  $\text{mg L}^{-1}$   $\text{O}_3$ , 2.32  $\text{mg L}^{-1}$  to each with three diffusers). Ozone exposure was calculated as the area under the ozone residual profiles. For the single diffuser control condition (Ctrl) the 1st order ozone decay rate was calculated, then the decay curve was extended and integrated until ozone had completely decayed.

### 3.3 Mechanistic implications for bromate formation

In wastewater, bromate is thought to primarily be formed through the *indirect* pathway, highlighted in Fig. 1, due to the relatively low ozone exposures and the higher concentrations of  $\cdot\text{OH}$  formed.<sup>20</sup> To test this, ammonium was added to plant B effluent with 0.035  $\text{mg L}^{-1}\text{-N}$  background  $\text{NH}_4^+$  from 0.5 to 1.1  $\text{O}_3$ :TOC (Fig. S2). Ammonium is a commonly used drinking water bromate suppression technique where  $\text{NH}_3$  and  $\text{HOBr}$  react to form  $\text{NH}_2\text{Br}$  which prevents Br from being further oxidized.<sup>41</sup> Addition of 1.5  $\text{mg L}^{-1}\text{-N}$  had a negligible impact on bromate formation in the control condition and no effect when  $\text{H}_2\text{O}_2$  was added. 1.5  $\text{mg L}^{-1}$  is considerably higher than what is typically used to control bromate in drinking water treatment and should be sufficient to quench any  $\text{HOBr}/\text{OBr}^-$  as  $\text{NH}_2\text{Br}$ .<sup>41</sup> This confirms that, as expected, bromate was formed only through the *indirect* pathway. This also shows that quenching  $\text{HOBr}/\text{OBr}^-$  was not responsible for bromate suppression by  $\text{H}_2\text{O}_2$  in this case.

Fig. 5 shows an example ozone residual profile collected on plant B comparing several dosing conditions. The addition of  $\text{H}_2\text{O}_2$  significantly increased ozone decay rate and greatly decreased the ozone exposure. Interestingly, the calculated ozone exposure for the three-diffuser condition with  $\text{H}_2\text{O}_2$  was slightly higher than with a single diffuser. However, it should be noted that increasing the number of dissolution zones increases the potential for interference in ozone residual measurements taken in the diffusion columns due to undissolved ozone in the gas bubbles. This trend was observed across tests and plants (Fig. 6), indicating that the reduction in local ozone concentration is more important than the reduction in ozone exposure with hydrogen peroxide addition. The reaction between  $\text{Br}\cdot$  and  $\text{O}_3$  controls bromate formation in this scenario, thus the ozone concentration determines whether  $\text{Br}\cdot$  reacts with ozone to form bromate or with organics to be reduced back to  $\text{Br}^-$ .

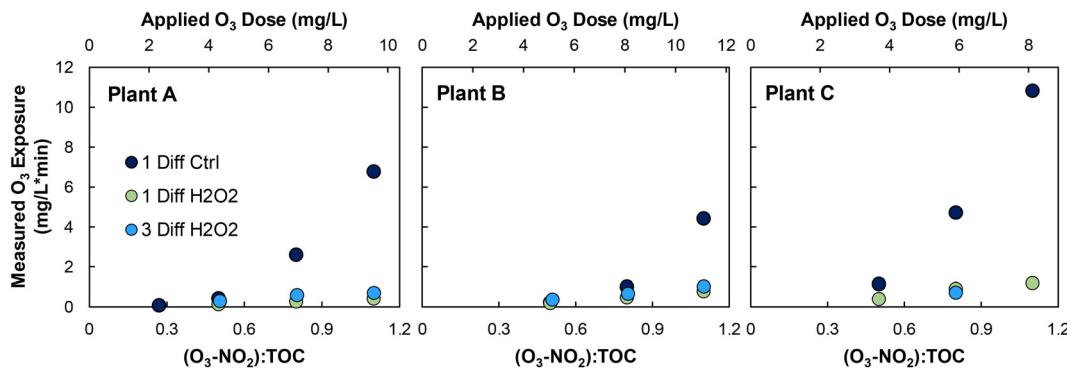


Fig. 6 Total ozone exposures calculated from ozone residuals collected in the tests presented in Fig. 1. Residuals were not collected for all tests in the three-diffuser condition for plant C.

### 3.4 Effects of water quality on BrO<sub>3</sub> formation and 1,4-dioxane removal

**3.4.1 pH.** Fig. 7A shows that bromate increased by a factor of two from pH 6 to 8 in the control condition in plant B effluent, while it increased 3.5 $\times$  in plant A effluent under similar conditions (Fig. S3). This increased sensitivity to pH may explain the higher bromate yields for plant A in Fig. 3. In the H<sub>2</sub>O<sub>2</sub> conditions with one diffuser, bromate increased similarly for one plant A test but was unaffected by pH in another (Fig. S3 and S4). For three diffusers, bromate increased slightly in plant B effluent and was stable or decreased in plant A effluent. Overall ·OH formation and exposure from 1,4-dioxane removal did not change with increasing pH, assuming that ·OH radical scavenging rates do not vary significantly.<sup>5</sup> saw that ·OH exposure increased substantially when pH was increased from 2.0 to 6.7 but only varied slightly between pH 6.7 and 7.9.

Ozone decay rate and exposure were extremely sensitive to pH. Ozone is generally much more reactive with the deprotonated forms of the organic moieties which control ozone decay such as phenol/phenolate,  $k_{O_3, \text{Phenol}} = 1300 \text{ M}^{-1} \text{ s}^{-1}$   $k_{O_3, \text{Phenolate}} = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $pK_a$  9.9.<sup>27,42</sup> Ozone also only reacts with the deprotonated HO<sub>2</sub><sup>-</sup> anion form of hydrogen peroxide. Thus, the effective reaction rate between hydrogen peroxide ( $k_{\text{obs}}$ , in Fig. 1) and

with many organics, varies by an order of magnitude for each pH unit. Ozone decay rate increased by a factor of 3.5 and 9.2 in the single diffuser control and H<sub>2</sub>O<sub>2</sub> conditions, respectively from pH 6 to 8 (Fig. S5).

Bromate formation has been shown to be highly sensitive to pH in drinking water.<sup>41,43</sup> However, there has been little study of the effects of pH on bromate formation in wastewater. In drinking water, the shift in HOBr/OBr<sup>-</sup>  $pK_a$  is thought to be partially responsible for decreasing bromate at lower pH. However, given that the direct oxidation of Br<sup>-</sup> to HOBr/OBr<sup>-</sup> is not as prevalent in wastewater ozonation conditions, it is more likely that the increased rate of ·OH generation increased the concentration of Br<sup>·</sup> formed that could then react with ozone. In samples collected in plant B effluent at 0.6 O<sub>3</sub>:TOC during testing described in Hogard *et al.*,<sup>44</sup> in the control condition bromate decreased from pH 7.8 to 8.4 while it continued to increase with H<sub>2</sub>O<sub>2</sub> addition (Fig. S6). This decrease may be due to the available ozone concentration decreasing too far to oxidize Br<sup>·</sup> further. The variability in individual trends of bromate with pH between conditions is difficult to entirely explain without a complete understanding of the complex competition kinetics between ozone, H<sub>2</sub>O<sub>2</sub>/HO<sub>2</sub><sup>-</sup>, bromide radical species, and organics. In bromide spike testing on plant C, bromate decreased by 17% on average when pH was suppressed from 7.0 to 6.6 (Fig. S7).

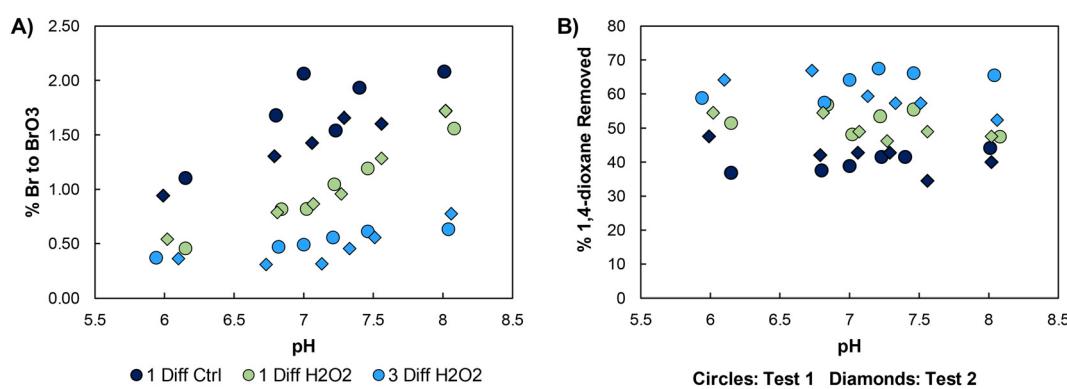


Fig. 7 A) Molar conversion of bromide to bromate and B) 1,4-dioxane removed in plant B secondary effluent at a fixed ozone dose of 0.8 (O<sub>3</sub>-NO<sub>2</sub>):TOC, 20 °C. Test 1: 8.56 mg L<sup>-1</sup> TOC, 0.163 mg L<sup>-1</sup> Br, Test 2: 9.8 mg L<sup>-1</sup> TOC, 0.365 mg L<sup>-1</sup> Br.



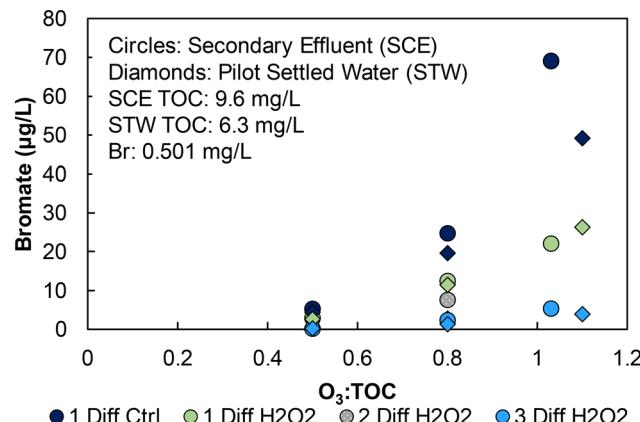


Fig. 8 Bromate formed with and without ACH coagulation at plant B.

**3.4.2 TOC and nitrite.** Fig. 8 shows that, when dosing on an  $\text{O}_3:\text{TOC}$  basis, lower applied doses in the lower TOC coagulated water decreased bromate slightly in the control condition while the difference was negligible in the  $\text{H}_2\text{O}_2$  conditions. Organics control the consumption of ozone and the formation and scavenging of hydroxyl radicals. Plant C had the lowest ozone demand and highest ozone exposure on both an applied dose and  $\text{O}_3:\text{TOC}$  basis as shown in Fig. 6. Comparing ozone exposure and decay between plants A and C at similar TOC, pH, and applied ozone dose in Fig. S8 (from the test shown in Fig. 4), this trend is still observed. Plant C had slightly lower specific UV absorbance (SUVA) of 1.77 vs. 2.0 and 1.98  $\text{mL mg}^{-1}$  for plants A and B, respectively. As a surrogate for aromatic compounds this may shed some light on the differences in ozone consumption between plants, though it is unclear if this difference is enough to be significant. Further tests looking at electron donating capacity, EDC, a general measure of the total phenolic content of the water,<sup>45,46</sup> and other tests to better understand the nature of organics and their role in bromate formation should be conducted.

In a test with three diffusers, when  $\text{NO}_2^-$  was spiked, both bromate formation and 1,4-dioxane removal decreased (Fig. S11), correcting for  $\text{NO}_2^-$  demand bromate formation

increased slightly ( $\sim 0.3 \mu\text{g L}^{-1}$ ) and 1,4-dioxane removal returned to nearly the initial removal. At the highest  $\text{NO}_2^-$  concentration,  $1.03 \text{ mg L}^{-1}\text{-N}$ , dosing the extra ozone for  $\text{NO}_2^-$  demand to the first diffuser was also tested. This resulted in slightly higher bromate formation and marginally improved 1,4-dioxane removal, though both were within the margin for analytical error. Overall, these results indicate that  $\text{NO}_2^-$  corrected  $\text{O}_3:\text{TOC}$  ratio would be a reasonable approach to targeting 1,4-dioxane removal, through the correlations do appear to be plant specific.

**3.4.3 Bromide.** With  $\text{H}_2\text{O}_2$  addition, bromate formation increased linearly with increasing bromide concentration (Fig. 9A and B). In one test at 1.1  $\text{O}_3:\text{TOC}$  (Fig. 9A), bromate formation exceeded the MCL at  $0.84 \text{ mg L}^{-1}\text{ Br}^-$  with three diffusers while four diffusers formed approximately 25% less bromate and would allow slightly higher bromide levels to be treated. Assuming the linear relationship between bromide and bromate was consistent, bromate would exceed the MCL at approximately  $1.5$  and  $1.75 \text{ mg L}^{-1}\text{ Br}^-$  with six or eight diffusers, respectively. This shows that bromate formation can be successfully controlled at extremely high bromide concentrations with reasonable  $\text{H}_2\text{O}_2$  doses for bromate suppression when using multi-point dissolution with increasing diffusion zones. This is promising for the feasibility of ozonation at plant C, which receives high bromide from significant saltwater infiltration. For the test shown in Fig. 9A, 1,4-dioxane removal decreased from 75 to 64% on average (data not shown) when bromide increased from  $0.40$  to  $2.37 \text{ mg L}^{-1}$  due to hydroxyl radical scavenging by bromide. A similar trend was observed at plant A (Fig. S9).

Fig. 9B shows that with a single diffuser without chemical addition, bromate formation increased and then leveled off with increasing bromide concentration, while bromate formation increased linearly with increasing bromide when  $\text{H}_2\text{O}_2$  was present. This may help explain why more bromate was formed in the single diffuser  $\text{H}_2\text{O}_2$  condition in plant C effluent (Fig. 3C and 4C). However, the mechanism at play is difficult to explain; ozone decay rate was identical between the lowest and highest bromide concentration, which was unexpected (Fig. S10). Although the reaction rate between

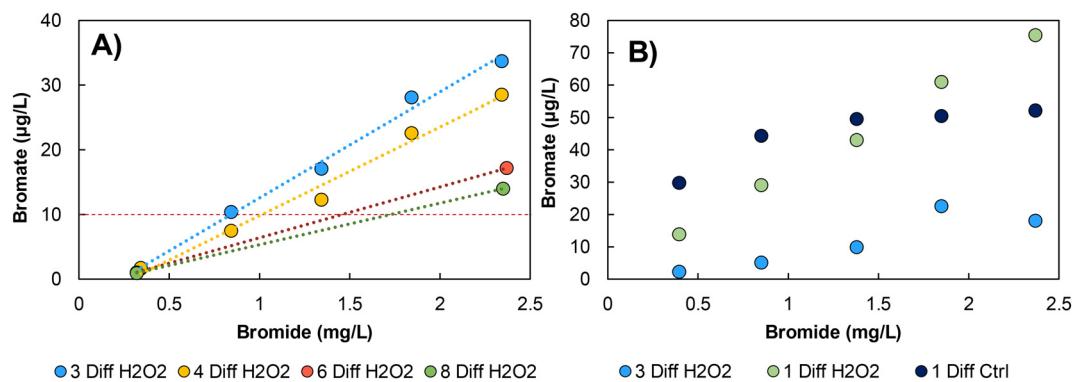


Fig. 9 A) Plant B bromide spike testing at 1.1 ( $\text{O}_3:\text{NO}_2^-$ ):TOC, 1:1  $\text{H}_2\text{O}_2:\text{O}_3$  with 3, 4, 6, & 8 diffusers and B) repeated bromide spike testing with a single diffuser and a no peroxide control condition.



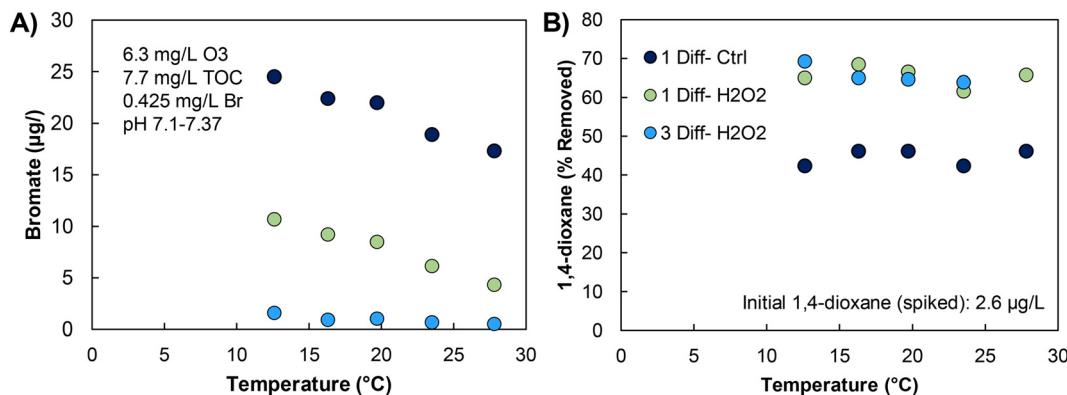


Fig. 10 A) Bromate formed and B) 1,4-dioxane removed in plant A effluent from 12–28 °C at 0.8 (O<sub>3</sub>-NO<sub>2</sub>):TOC. 4.25 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> when used (1:1 H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub>).

ozone and bromide (Fig. 1,  $k_{Br+O_3} = 160 \text{ M}^{-1} \text{ s}^{-1}$ ) is relatively slow, several mg L<sup>-1</sup> Br<sup>-</sup> should increase ozone decay rate. The Br<sup>-</sup>-OH reaction shown in Fig. 1 is actually a two-step reaction with BrOH<sup>-</sup> as an intermediate product which then dissociates to form Br<sup>·</sup>. BrOH<sup>-</sup> can react with Br<sup>-</sup> to form Br<sub>2</sub><sup>-</sup> which does not react with ozone. However, modeling of the O<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> process by Mortazavi *et al.*<sup>39</sup> showed that these reactions were unaffected below 8 mg L<sup>-1</sup> Br<sup>-</sup> (100 µM).

**3.4.4 Temperature.** At a fixed ozone dose of 0.8 O<sub>3</sub>:TOC, bromate formation decreased with increasing temperature while 1,4-dioxane removal was unaffected (Fig. 10). With three diffusers, bromate decreased from 1.59 to 0.51 µg L<sup>-1</sup> when increasing from 12 to 28 °C. A similar trend in bromate formation with temperature was observed in plant B effluent using a single diffuser, with and without H<sub>2</sub>O<sub>2</sub>, in samples collected along with disinfection testing described in Hogard *et al.*<sup>44</sup> (Fig. S12).

It is difficult to conclude precisely why bromate formation decreased with increasing temperature. Farzaneh *et al.*<sup>47</sup> saw an increase and then decrease in bromate when increasing temperature from 25 to 40 °C at ~0.27 O<sub>3</sub>:TOC in batch testing of tertiary effluent. In drinking water literature there are reports of both increased and decreased bromate formation for the same applied ozone dose with increasing temperature.<sup>48–50</sup> Of the bromate formation reactions in Fig. 1, Arrhenius information is only available for the reaction of ozone and bromide.<sup>19</sup> The fast ·OH and O<sub>3</sub> reactions involved in the *indirect* bromate formation pathway are likely less affected by temperature due to their lower activation energies.<sup>27</sup> The slower reactions with bulk organics which control the overall ozone decay rate do appear to be affected by temperature where the ozone decay rate increased by a factor of 3.1 and 4.0 in the single diffuser control and H<sub>2</sub>O<sub>2</sub> conditions, respectively. Therefore, there was less ozone available to react with Br<sup>·</sup> to form bromate. From a practical standpoint, given the low H<sub>2</sub>O<sub>2</sub> doses required for bromate control at plants A and B, it is likely that H<sub>2</sub>O<sub>2</sub> dose could be decreased significantly or even turned

off during the summer months depending on oxidation objectives.

## 4. Conclusions

Multi-point ozone dissolution was tested on three high bromide wastewater effluents. Compared to the single diffuser configuration, increasing the number of diffusion zones decreased bromate formation and significantly reduced the hydrogen peroxide dose required for bromate suppression. These results show that with ozone dissolution systems and contactors designed around the use of H<sub>2</sub>O<sub>2</sub>, bromate can be adequately controlled in high bromide wastewater effluents.

- Hydrogen peroxide addition significantly increased ·OH exposure and 1,4-dioxane removal. 0.5 log removal could be achieved at 0.8–1.0 O<sub>3</sub>:TOC with 1:1 molar H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub>. 0.5 log 1,4-dioxane removal was not observed without H<sub>2</sub>O<sub>2</sub> addition at the ozone doses tested ( $\leq 1.4$  O<sub>3</sub>:TOC).

- Splitting the ozone dose between three diffusers reduced the required H<sub>2</sub>O<sub>2</sub> dose to achieve the same level of bromate formation as a single diffuser by as much as 90%. Increasing to as many as eight diffusers continued to decrease bromate formation. This was most beneficial at higher ozone doses and bromide concentrations.

- At two of the three plants, H<sub>2</sub>O<sub>2</sub> addition decreased bromate formation with a single diffuser. While at the third, bromate formation increased at the lower H<sub>2</sub>O<sub>2</sub> doses ( $\leq 0.5$  H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub>) and required  $> 2.0$  H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> to reduced bromate formation to below the control condition. The exact cause of this increase is still unclear and warrants further study.

- Bromate formation increased with increasing pH while 1,4-dioxane removal was unchanged. With H<sub>2</sub>O<sub>2</sub> addition, bromate formation was less affected by pH. Ozone decay and exposure were highly sensitive to pH, both with and without H<sub>2</sub>O<sub>2</sub>.

- Bromide spike tests showed that three-point dissolution could control bromate to below the MCL at a moderately high ozone dose of 1.1 O<sub>3</sub>:TOC at up to approximately 0.7 mg L<sup>-1</sup>



$\text{Br}^-$ . Increasing to four, six or eight diffusers would allow waters with even higher bromide concentrations to be ozonated.

- Bromate formation decreased at higher temperatures while  $\cdot\text{OH}$  exposure was unaffected.

## Conflicts of 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.

## Data availability

Supplementary information: Additional figures and data. See DOI: <https://doi.org/10.1039/D4EW00627E>.

Data will be made available on request.

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