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Critical Review

Critical Review on Bromate Formation during Ozonation and Control Options for Its Minimization

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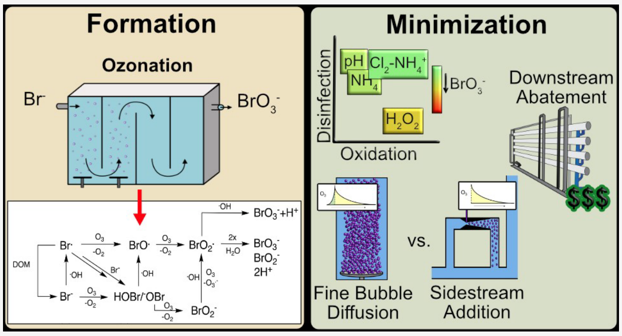

ABSTRACT: Ozone is a commonly applied disinfectant and oxidant in drinking water and has more recently been implemented for enhanced municipal wastewater treatment for potable reuse and ecosystem protection. One drawback is the potential formation of bromate, a possible human carcinogen with a strict drinking water standard of 10 μg/L. The formation of bromate from bromide during ozonation is complex and involves reactions with both ozone and secondary oxidants formed from ozone decomposition, i.e., hydroxyl radical. The underlying mechanism has been elucidated over the past several decades, and the extent of many parallel reactions occurring with either ozone or hydroxyl radicals depends strongly on the concentration, type of dissolved organic matter (DOM), and carbonate. On the basis of mechanistic considerations, several approaches minimizing bromate formation during ozonation can be applied. Removal of bromate after ozonation is less feasible. We recommend that bromate control strategies be prioritized in the following order: (1) control bromide discharge at the source and ensure optimal ozone mass-transfer design to minimize bromate formation, (2) minimize bromate formation during ozonation by chemical control strategies, such as ammonium with or without chlorine addition or hydrogen peroxide addition, which interfere with specific bromate formation steps and/or mask bromide, (3) implement a pretreatment strategy to reduce bromide and/or DOM prior to ozonation, and (4) assess the suitability of ozonation altogether or utilize a downstream treatment process that may already be in place, such as reverse osmosis, for post-ozone bromate abatement. A one-size-fits-all approach to bromate control does not exist, and treatment objectives, such as disinfection and micropollutant abatement, must also be considered.

KEYWORDS: *bromate, ozonation, human carcinogen, dissolved organic matter*

■ INTRODUCTION

Ozone is applied as a disinfectant and oxidant during drinking water treatment, with hundreds of full-scale treatment plants worldwide.[1] As interest in water reuse and ecological protection of waterways grows in the United States and Europe, ozonation is increasingly included in advanced wastewater treatment processes for the oxidation of micropollutants by ozone and hydroxyl radicals ($^{\bullet}$OH).[1,2] During ozonation of bromide-containing waters, oxidation of bromide by ozone and $^{\bullet}$OH leads to bromate formation, which is a human and ecological health concern.

This Critical Review of the current knowledge of bromate will cover the following aspects: (i) toxicity of bromate, (ii) sources of bromide in natural waters and wastewaters, (iii) analytical methods for bromate determination, (iv) kinetics and mechanisms of bromate formation, (v) theoretical and empirical modeling of bromate formation, and (vi) bromate mitigation strategies implemented before, during, and after ozonation.

■ TOXICOLOGICAL ASPECTS OF BROMATE

Bromate was classified as a possible human carcinogen in the 1990s and is regulated to a maximum contaminant level of 10 μg/L by several regulatory agencies.[3,4] This stringent limit is based on toxicological studies conducted on rodents[5−7] and subsequent risk assessments conducted by the U.S. Environmental Protection Agency (USEPA) and the World Health Organization (WHO).[8,9] These studies have shown that exposure to bromate may result in cancer in kidneys, thyroid, and testicular mesothelium of rats.[7] Although bromate is regulated as a probable genotoxic carcinogen, there is evidence of a nongenotoxic mode of action.[10,11] Genotoxic effects have

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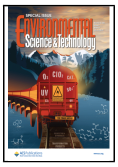

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been shown to result from oxidative damage to DNA at relatively high levels of exposure to bromate, whereas nongenotoxic effects, including apoptosis (cell death) and mutation, can result at lower bromate concentrations.[10] Studies have also shown the reduction of bromate to bromide in simulated gastric solutions, suggesting that regulatory limits might be set conservatively low.[12] The strict human health standard for bromate has limited the applicability of ozone for disinfection/oxidation in both water and enhanced wastewater treatment.

Bromate has also demonstrated potential ecological impacts. Lethal concentrations (LC_{50}) of bromate in the range of 31−2258 mg/L for different fish species have been reported.[13,14] With a safety factor of 10, a long-term bromate exposure limit of 3 mg/L was proposed to protect the most sensitive aquatic organisms.[13] Bromate exposure tests with *Ceriodaphnia dubia* resulted in a more stringent acute and chronic standard of 50 μg/L.[15,16]

BROMIDE OCCURRENCE AND SOURCES

Bromide is naturally occurring in geological structures such as limestone, granite, and shale, at concentrations ranging between 0.3 and 24 mg/kg.[17] Typically, bromide in surface water results from geogenic sources,[17] but other sources include seawater intrusion and anthropogenic sources.[18,19] Anthropogenic sources of bromide include industrial point discharges, municipal waste incinerators, landfills, chemical plants, coal-fired power plants, private swimming pools, and hydraulic fracturing.[19−22] Median bromide levels in drinking water sources (groundwaters and surface waters) were in the range of 30−80 μg/L on the basis of U.S. surveys; however, concentrations have been observed in the range of hundreds of microgram to milligrams per liter.[23,24]

A bromide concentration threshold of ∼100 μg/L was proposed for drinking water disinfection with ozone to avoid a violation of the drinking water standard for bromate.[25] This is only a rough estimate, because bromate formation largely depends on other treatment goals and the water matrix.[26] In a specific water source, the bromide threshold level may be significantly different, and therefore, site specific tests should be performed.[26] Bromide levels in wastewater effluents can be significantly higher, with median levels reported around 230 μg/L,[23] and higher levels of ≤50 mg/L have been reported.[22] The elevated bromide levels in wastewaters magnify the challenges pertaining to bromate control during ozonation for potable reuse applications and ecosystem protection scenarios. A full summary of bromide occurrence is outside the scope of this review; however, this topic has been evaluated in numerous previous studies.[17,20,22−24,27−32]

BROMATE MEASUREMENT

Bromate is primarily analyzed by ion chromatography with conductivity detection (IC-CD) with method reporting limits (MRL) of 4−5 μg/L.[33−37] Detection of bromate by postcolumn reactions followed by ultraviolet (UV) measurement (IC-PCR) avoids interference from chloride and sulfate and increases sensitivity. An MRL of ≲1 μg/L is possible with this approach.[38−40] Other methods use ion chromatography coupled with inductively coupled plasma mass spectrometry (IC-ICP-MS), (tandem) mass spectrometry (IC-MS and IC-MS/MS), or liquid chromatography-tandem triple quadrupole mass spectrometry (LC-MS/MS).[40−44] MS-based methods have sub-microgram per liter MRLs. For laboratory studies on bromate formation, or monitoring in practice, IC-PCR or IC/LC-MS methods should be applied to have MRLs far below the drinking water standard of 10 μg/L. There has been limited success for online bromate measurements. One approach, which utilizes fluorescence detection of trifluoperazine (TFP), has been examined and showed promise; however, further long-term experience is needed with such systems.[45,46]

For sample collection, oxidant quenching should be carried out to avoid continuing bromate formation during storage. Quenching agents, such as indigo trisulfonate, thiosulfate, sulfite, buten-3-ol, or cinnamic acid, can be applied.[42,47] Proper preservation and the proper storage temperature (<6 °C) result in holding times of approximately one month without sample deterioration.[34]

BROMATE FORMATION DURING OZONATION

Overview of Pathways. *Ozone Reactions.* Acidic solutions containing ozone and bromide were investigated in the 1940s with the goal of measuring Br_2 formation.[48] This reaction was confirmed at circumneutral pH with the formation of $HOBr/OBr^-$, which is the hydrolysis product of Br_2.[49,50] This is the first step in bromate formation with ozone (eq 1):

$$O_3 + Br^- \rightarrow OBr^- + O_2 \tag{1}$$

Two second-order rate constants for reaction 1 were reported: $k = 160\ M^{-1}\ s^{-1}$ at 20 °C[49] or $k = 258\ M^{-1}\ s^{-1}$ at 25 °C.[50] With these moderate second-order rate constants, calculated half-life times of bromide are in the range of 2−4 min for an ozone concentration of 1 mg/L. Therefore, for disinfection processes with a substantial ozone exposure, significant extents of OBr^- can be formed. During oxidation of micropollutants, often no or low ozone residual concentrations are present and therefore OBr^- formation will be minor.[22]

OBr^- is in equilibrium with HOBr with a pK_a of 8.8[51] (eq 2):

$$OBr^- + H^+ \rightleftarrows HOBr \tag{2}$$

This high pK_a of HOBr is crucial for bromate formation with ozone, because HOBr reacts very slowly with ozone ($k \leq 10^{-2}\ M^{-1}\ s^{-1}$[49]), whereas OBr^- has a moderate reactivity ($k = 100\ M^{-1}\ s^{-1}$ at 20 °C[49]) (eq 3):

$$O_3 + OBr^- \rightarrow BrO_2^- + O_2 \tag{3}$$

In addition to reaction 3, the attack of ozone on OBr^- can also proceed through a second faster reaction, which is a reduction of OBr^- back to bromide ($k = 330\ M^{-1}\ s^{-1}$ at 20 °C[49]) (eq 4):

$$O_3 + OBr^- \rightarrow Br^- + 2\,^1O_2 \tag{4}$$

Paradoxically, this is a reductive process occurring during ozonation. Similar reactions occur during the ozonation of OCl^- and Mn^{2+}.[52,53]

The last reaction en route to bromate is an oxidation of bromite (BrO_2^-), which has been suggested to be an oxygen-transfer reaction ($k > 10^5\ M^{-1}\ s^{-1}$ at 20 °C[49]) (eq 5):

$$O_3 + BrO_2^- \rightarrow BrO_3^- + O_2 \tag{5}$$

However, more recently it was demonstrated that reaction 5 proceeds via an electron transfer ($k = 8.9 \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C[54]) (eq 6):

$$O_3 + BrO_2^- \rightarrow BrO_2^{\bullet} + O_3^{\bullet -} \tag{6}$$

Bromine dioxide ($BrO_2^{\bullet}$) undergoes a self-reaction and a disproportionation[54,55] according to eqs 7 and 8:

$$2BrO_2^{\bullet} \rightleftarrows Br_2O_4 \qquad (7)$$

$$Br_2O_4 + H_2O \rightarrow BrO_2^- + BrO_3^- + H_2O \qquad (8)$$

An overall second-order rate constant from bromine dioxide to bromate has been estimated as $k = 5 \times 10^7\ M^{-1}\ s^{-1}$ at 10 °C.[54]

Hydroxyl Radical Reactions. In the original studies on bromate formation, the role of $^{\bullet}OH$ was not considered.[49] However, it can play a major role at various levels of bromate formation during ozonation.[56]

Bromide can be oxidized by $^{\bullet}OH$ to bromine radicals ($Br^{\bullet}$) in a two-step reaction with an equilibrium[57] (eqs 9 and 10):

$$^{\bullet}OH + Br^- \rightleftarrows BrOH^{\bullet-} \qquad (9)$$

$$BrOH^{\bullet-} \rightleftarrows Br^{\bullet} + {}^-OH \qquad (10)$$

The second-order rate constant for reaction 9 is $1.06 \times 10^{10}\ M^{-1}\ s^{-1}$;[58] however, due to the equilibrium character of eqs 9 and 10, an overall second-order rate constant of $k = 1.1 \times 10^9\ M^{-1}\ s^{-1}$ for the net reaction of bromide to $Br^{\bullet}$ can be estimated for bromide concentrations of ≤1 mg/L[59] (eq 11):

$$^{\bullet}OH + Br^- \rightarrow Br^{\bullet} + {}^-OH \qquad (11)$$

One of the main sinks of $Br^{\bullet}$ is its reaction with bromide, with a second-order rate constant (k) of $\approx 10^{10}\ M^{-1}\ s^{-1}$ for the forward and $6.6 \times 10^3\ M^{-1}\ s^{-1}$ for the reverse reaction[1] (eq 12):

$$Br^{\bullet} + Br^- \rightleftharpoons Br_2^{\bullet-} \qquad (12)$$

$Br_2^{\bullet-}$ can lead to the formation of Br_2 over several equilibria and disproportionation reactions,[1] and Br_2 is then hydrolyzed to HOBr under typical water treatment conditions.[51] This pathway is also crucial for bromate formation in systems with only $^{\bullet}OH$ (without ozone) as was demonstrated with γ-radiolysis experiments.[60,61] Because $HOBr/OBr^-$ is a decisive intermediate, bromate is not formed in UV-based advanced oxidation in the presence of hydrogen peroxide (H_2O_2) (e.g., UV/H_2O_2), because H_2O_2 reduces $HOBr/OBr^-$ back to bromide. This is not the case for ozone-based advanced oxidation (see Hydrogen Peroxide).[62] Also, $BrOH^{\bullet-}$, which is formed from the reaction of $^{\bullet}OH$ with Br^- (eq 9), reacts with bromide, leading to $Br_2^{\bullet-}$ and the ensuing reactions.[1,57]

$HOBr/OBr^-$, which is formed from the oxidation of bromide with ozone or $^{\bullet}OH$, can further react with $^{\bullet}OH$ with second-order rate constants of $2 \times 10^9\ M^{-1}\ s^{-1}$ ($k_{OH,HOBr}$) and $4.5 \times 10^9\ M^{-1}\ s^{-1}$ (k_{OH,OBr^-})[63] (eqs 13 and 14):

$$^{\bullet}OH + HOBr \rightarrow BrO^{\bullet} + H_2O \qquad (13)$$

$$^{\bullet}OH + OBr^- \rightarrow BrO^{\bullet} + {}^-OH \qquad (14)$$

Bromine monoxide ($BrO^{\bullet}$) can also be formed from the reaction of hypobromite with carbonate radicals ($k = 4.3 \times 10^7\ M^{-1}\ s^{-1}$[63]). This reaction is relevant, because of the higher steady-state concentrations of carbonate radicals compared to that of $^{\bullet}OH$.[64]

$BrO^{\bullet}$ undergoes disproportionation with the formation of hypobromite and bromite ($k = 4.9 \times 10^9\ M^{-1}\ s^{-1}$[63]) (eq 15):

$$2BrO^{\bullet} + H_2O \rightarrow OBr^- + BrO_2^- + 2H^+ \qquad (15)$$

Bromite, which also reacts with ozone (see above), can react further with $^{\bullet}OH$ to afford bromine dioxide ($BrO_2^{\bullet}$) ($k = 1.9 \times 10^9\ M^{-1}\ s^{-1}$[63]) (eq 16):

$$BrO_2^- + {}^{\bullet}OH \rightarrow BrO_2^{\bullet} + {}^-OH \qquad (16)$$

An analogues reaction (eq 16) also occurs with the carbonate radical ($k = 1.1 \times 10^8\ M^{-1}\ s^{-1}$[63]). Bromine dioxide can then react further to afford bromate according to reactions 7 and 8 or with $^{\bullet}OH$ ($k = 2 \times 10^9\ M^{-1}\ s^{-1}$[65]) (eq 17):

$$BrO_2^{\bullet} + {}^{\bullet}OH \rightarrow BrO_3^- + H^+ \qquad (17)$$

Bromine Radical Reactions. Bromine radicals (see eqs 9 and 10) can undergo the following reactions: (i) oxidation by ozone, (ii) reaction with bromide, and (iii) reaction with dissolved organic matter (DOM).

(i) On the basis of a combination of γ-radiolysis and tailored ozonation experiments, it was estimated by kinetic modeling that $Br^{\bullet}$ reacts with ozone to afford bromine monoxide ($BrO^{\bullet}$) with a k of $\approx 1.5 \times 10^8\ M^{-1}\ s^{-1}$[61] (eq 18), the same product that is also formed by eqs 13 and 14:

$$O_3 + Br^{\bullet} \rightarrow BrO^{\bullet} + O_2 \qquad (18)$$

Bromine monoxide then disproportionates according to eq 15. This pathway can lead to bromate during the O_3/H_2O_2 advanced oxidation process (AOP).

(ii) According to eq 12, $Br^{\bullet}$ is in equilibrium with $Br_2^{\bullet-}$ as a potential sink. Figure S1 shows the $Br^{\bullet}/Br_2^{\bullet-}$ equilibrium concentration ratios as a function of bromide concentration. For a bromide concentration of 1 μM (80 μg/L), ∼87% is present as $Br^{\bullet}$ and ∼13% as $Br_2^{\bullet-}$. The $Br^{\bullet}/Br_2^{\bullet-}$ concentration ratio is ∼1 at 500 μg/L bromide. Therefore, for low to moderate bromide levels, $Br^{\bullet}$ will always dominate and therefore contribute to further reactions with ozone.

(iii) Another important sink for $Br^{\bullet}$ is DOM, with second-order rate constants (k) in the range of $1.4{-}4.2 \times 10^8\ M_C^{-1}\ s^{-1}$ for DOM isolates and real waters.[66,67] Experiments with a preozonated DOM isolate showed that the second-order rate constant with $Br^{\bullet}$ did not change significantly, which implies a constant consumption of $Br^{\bullet}$ by DOM during ozonation.[67]

Reactions of $Br^{\bullet}$ with organic compounds proceed mainly by electron transfer,[66−68] shown for DOM in eq 19:

$$Br^{\bullet} + DOM \rightarrow Br^- + DOM^{\bullet+} \qquad (19)$$

It has been demonstrated that a minor fraction may proceed by an addition of bromine to the ensuing brominated products.[67]

On the basis of the second-order rate constants for the reactions of $Br^{\bullet}$ with ozone and DOM, the initial fraction of $Br^{\bullet}$ reacting with either constituent can be calculated as a function of the specific ozone dose (milligrams of O_3 per milligram of DOC) (eq 20 and Figure 1):

$$f(O_3 + Br^{\bullet}) = \frac{k_{O_3+Br^{\bullet}}[O_3]}{k_{O_3+Br^{\bullet}}[O_3] + k_{DOM+Br^{\bullet}}[DOC]} \qquad (20)$$

Figure 1 shows that for typically applied specific ozone doses (0.2−1.0 g of O_3/g of DOC), the initial fraction of $Br^{\bullet}$ reacting with ozone can account for ≤50% (DOC = 5 mg/L).

Bromate Formation Mechanism. On the basis of the reactions discussed above, a bromate formation mechanism including both ozone and $^{\bullet}OH$ can be compiled (Figure 2).

It is evident from Figure 2 that bromate formation is a complex reaction mechanism occurring during ozonation, because of the relevance of both ozone and $^{\bullet}OH$ at most reaction steps. The mechanism is compiled on the basis of

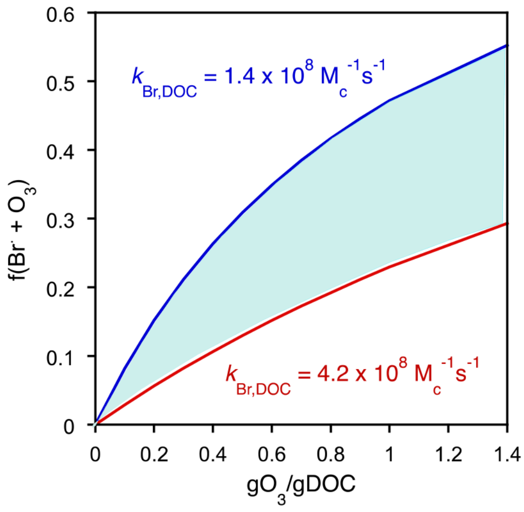

Figure 1. Fraction of the reaction of ozone with the bromine radical as a function of the specific ozone dose (the initial ozone dose is taken for the calculations). The blue and red curves represent the lower and higher limits, respectively, of the second-order rate constant for the reaction of Br$^\bullet$ with DOM. The colored area represents the range of the fraction *f*(Br$^\bullet$ + O_3) (eq 20) for the lower or higher second-order rate constants for the Br$^\bullet$–DOM reaction (second-order rate constants were obtained from ref 66) (DOC = 5 mg/L).

several key papers[47,49,56,59,61,69−72] and was also discussed in a previous publication.[1] This reaction mechanism was previously categorized into three main pathways. (i) The direct–direct (O_3) pathway consists of ozone-controlled bromate formation. (ii) The direct–indirect ($^\bullet$OH) pathway comprises an oxidation of bromide to HOBr/OBr$^-$ by ozone followed by a further oxidation by $^\bullet$OH. (iii) The indirect–indirect pathway consists of a $^\bullet$OH-dominated pathway.[73] Even though this approach can help as an orientation in the mechanism, it neglects that most reaction steps depend on the $^\bullet$OH/O_3 concentration ratio and the corresponding second-order rate constants. This ratio is water specific and depends on the specific ozone dose. To overcome this problem, the R_{ct} concept was developed, which allows for the determination of the $^\bullet$OH/O_3 concentration ratio by a relatively simple procedure.[74−77] This approach has also been applied to determine the ozonation transformation products of micropollutants.[78,79] During ozonation, typical concentration ratios (R_{ct}) of $^\bullet$OH and O_3 are on the order of 10^{-6}–10^{-9}. Figure 3 shows the fractions of reactions proceeding by O_3 or $^\bullet$OH for various bromine species (Br$^-$, HOBr/OBr$^-$, and BrO_2^-) as a function of R_{ct}.

Figure 3 illustrates that during the initial phase (second range) of ozonation (R_{ct} values as high as 10^{-6}[80]), reactions of $^\bullet$OH with bromide and HOBr/OBr$^-$ dominate over ozone reactions. For the later phases of ozonation ($R_{ct} > 10^{-7}$), bromide oxidation occurs mainly by ozone and, depending on the pH, the fraction of the further reaction of HOBr/OBr$^-$ with ozone making up between 10% and 80%. For bromite, ozone always outcompetes $^\bullet$OH for the further oxidation to bromate.

Water Quality Considerations. *Role of pH.* pH plays a decisive role in bromate formation; first and most importantly, it is crucial for ozone chemistry. At low pH, ozone is more stable and the formation of $^\bullet$OH is slow, which is demonstrated by 40 times lower R_{ct} values at pH 6 than at pH 9.[1,74] Such conditions are ideal for disinfection because high levels of ozone exposure are achieved with limited formation of $^\bullet$OH. Under such conditions, mainly HOBr is formed from the reaction of ozone with bromide, and it is not further oxidized by ozone due to the low reactivity of HOBr with ozone (see above). Even though the oxidation of HOBr by $^\bullet$OH has a reasonable second-order rate

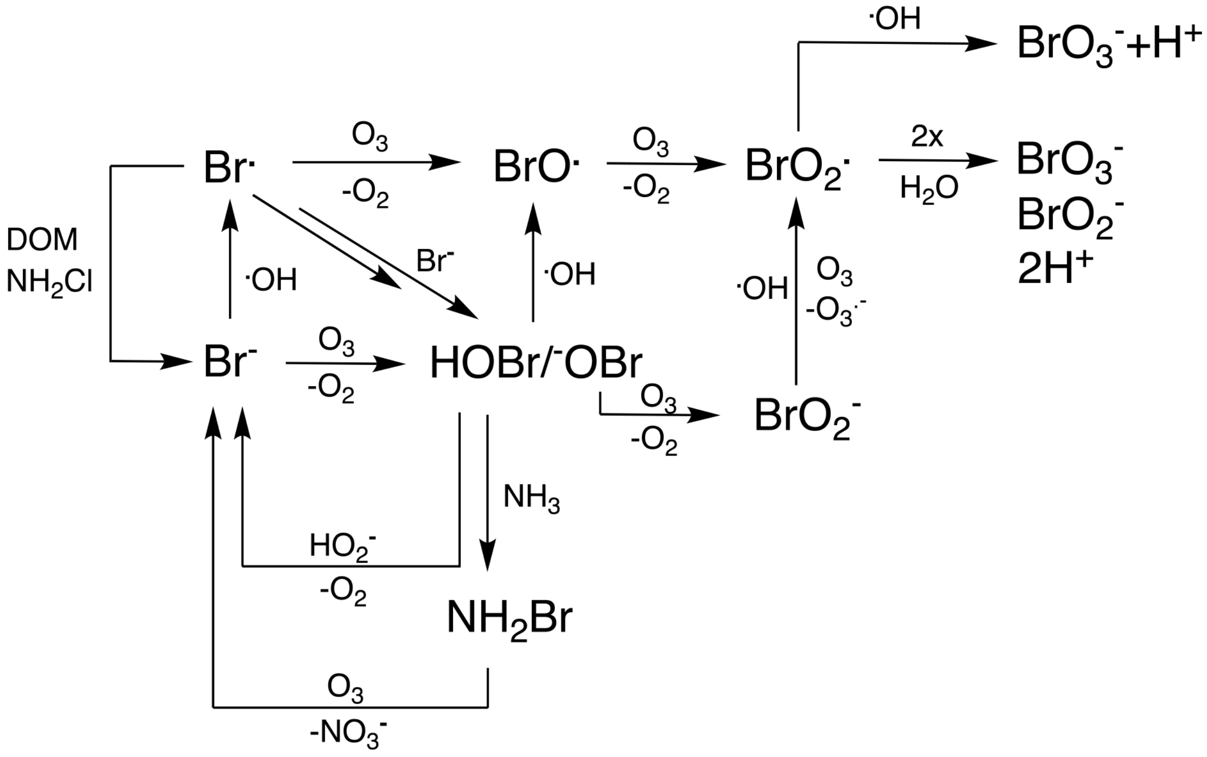

Figure 2. Simplified mechanism for bromate formation during ozonation of bromide-containing waters. Adapted from and expanded on the basis of a previous study.[1] Reactions of HOBr/OBr$^-$ with hydrogen peroxide and ammonia are also included.

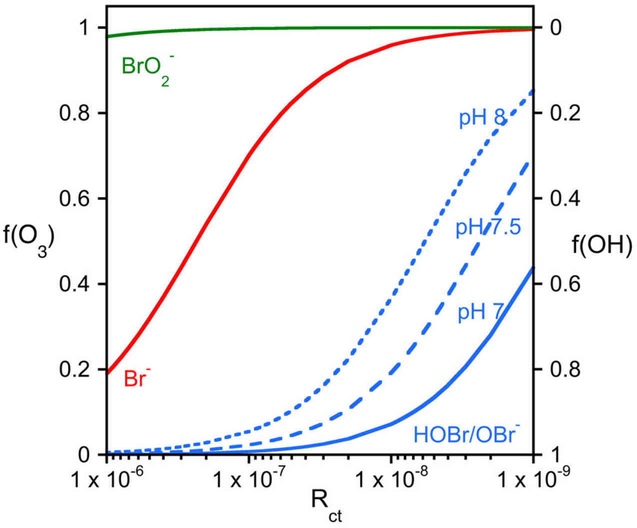

Figure 3. Fractions of reactions of Br^-, $HOBr/OBr^-$, and BrO_2^- occurring with ozone or $^\bullet OH$ as a function of R_{ct} in the range of 10^{-6}–10^{-9} ($^\bullet OH/O_3$ concentration ratio). Note that the *X*-axis and the second *Y*-axis are reversed.

constant, its oxidation by this pathway is slow because of the low transient $^\bullet OH$ concentrations at low pH.[47,74] The effect of pH on bromate formation has been demonstrated (e.g., during the ozonation of Seine River water with a bromide concentration of 60 μg/L) for which bromate concentrations of 4 and 9 μg/L were obtained at pH 6 ($R_{ct} = 2.9 \times 10^{-9}$) and pH 8 ($R_{ct} = 9.0 \times 10^{-9}$), respectively, for an ozone exposure of 10 mg L^{-1} min^{-1}.[47] pH depression can be applied as a bromate mitigation strategy during disinfection with ozone; at lower pH values, a better disinfection efficiency can be achieved with a lower level of bromate formation (see Mitigation).

Temperature. Temperature affects bromate formation at two levels: (i) faster reactions of bromide and transient bromine species[50] with ozone and $^\bullet OH$ and (ii) faster decomposition of ozone.[74] The only information about the effect of temperature on the oxidation of bromine species is related to the oxidation of bromide by ozone, with second-order rate constants of 258 and 97 M^{-1} s^{-1} at 25 and 5 °C, respectively.[50] The effect of temperature on R_{ct} is quite significant with an approximately 10-fold increase from 6.0×10^{-9} to 8.5×10^{-8} from 5 to 35 °C, respectively, for the ozonation of Lake Zurich water at pH 8. For a given ozone exposure, this leads to much higher level of bromate formation at higher temperatures, if the enhanced inactivation of microorganisms at higher temperatures is not considered.[81] Therefore, a temperature correction for disinfection should be implemented for ozone dosage control to achieve an ozone exposure, which guarantees a certain inactivation of target organisms.[82] This approach helps to save on ozone production and mitigates bromate formation. The overall benefit is difficult to predict, because only a few activation energies of the involved reactions (bromate formation, ozone decay, and inactivation of microorganisms) are known.

Dissolved Organic Matter. The effect of DOM on bromate formation is threefold: (i) quenching transient bromine species, (ii) scavenging ozone and $^\bullet OH$, and (iii) influencing the R_{ct}.

(i) HOBr can react with DOM moieties, such as phenols, β-dicarbonyl compounds, and amines.[47,51,83,84] Except for the amines, ozone also reacts quickly with such HOBr-quenching moieties, and therefore, they will not persist to react with HOBr.[1,85] It has been shown that the concentration of Br(+I) (sum of HOBr and bromamines) remains fairly constant during ozonation.[47] The reactivities of organic bromamines that might be present are 2−3 orders of magnitude lower with phenolic moieties than with HOBr, and therefore, the formation of bromoorganic compounds is also not expected from this pathway.[84]

(ii) Scavenging of ozone and $^\bullet OH$ is a major factor affecting ozonation processes. However, because ozonation has a certain oxidation/disinfection target, typical ozone doses are adapted to DOC concentrations to compensate for the oxidant demand. In this context, the specific ozone dose (milligrams of O_3 per milligram of DOC) is decisive for bromate formation. It has been demonstrated during wastewater ozonation that bromate formation is initiated at specific ozone doses of $\gtrsim$0.5 mg of O_3/mg of DOC.[22] Under these conditions, the ozone residual is high enough for reactions with bromide and $Br^\bullet$, and therefore, bromate can be formed.

(iii) The effect of DOM type on R_{ct} is probably the most important factor influencing bromate formation. In a study of 12 groundwaters and lake waters, it was shown that the R_{ct} values vary over 2 orders of magnitude.[75] Part of this effect is also due to varying carbonate levels (see the next section). Nevertheless, this shows that the indirect effect of DOM on bromate formation can be very significant.

Carbonate Alkalinity. Carbonate/bicarbonate reacts moderately with $^\bullet OH$ to afford carbonate/bicarbonate radicals.[86,87] This reaction can influence bromate formation on two levels, (i) reactions of carbonate radical with bromine species and (ii) quenching of $^\bullet OH$, thereby influencing R_{ct}.

(i) $^\bullet OH$ scavenging by carbonate depends on the pH ($k_{OH,HCO_3^-} = 8.5 \times 10^6$ M^{-1} s^{-1}; $k_{OH,CO_3^{2-}} = 3.9 \times 10^8$ M^{-1} s^{-1})[86,87] and the DOC concentration, because DOM is typically the main $^\bullet OH$ scavenger during the ozonation of real waters. Basically, carbonate scavenging affects the R_{ct}, and this in turn has a significant effect on bromate formation (see above). It has been shown during the ozonation of Lake Zurich water by varying the carbonate levels at pH 8 (15 °C) from 0 to 2.5 mM that R_{ct} decreases from 1.25×10^{-7} to 1.5×10^{-8}.[74] The influence of such changes on bromate formation is difficult to assess, because of the role of carbonate radicals as oxidants, which increase, while R_{ct} decreases. More systematic studies are necessary to assess these counteracting effects.

(ii) It has been reported that carbonate radicals can react with bromide with a second-order rate constant of $<5 \times 10^5$ M^{-1} s^{-1}:[88]

$$Br^- + CO_3^{\bullet -} \rightarrow Br^\bullet + CO_3^{2-} \tag{21}$$

This reaction is in equilibrium with the back reaction with second-order rate constants of 2×10^6 and 1×10^6 M^{-1} s^{-1} for carbonate and bicarbonate, respectively:[88]

$$Br^\bullet + CO_3^{2-} \rightarrow Br^- + CO_3^{\bullet -} \tag{22}$$

$$Br^\bullet + HCO_3^- \rightarrow Br^- + HCO_3^\bullet \tag{23}$$

Because the bicarbonate concentration in natural waters is typically in the millimolar range, the first-order rate constant for the back reaction will be orders of magnitude higher than that for the forward reaction, and therefore, oxidation of bromide by carbonate radical is negligible.

Oxidation of OBr^- by the carbonate radical occurs with a second-order rate constant of 4.3×10^7 M^{-1} s^{-1}:[86]

$$OBr^- + CO_3^{\bullet -} \rightarrow BrO^\bullet + CO_3^{2-} \tag{24}$$

This reaction seems to be relevant, because significant differences in bromate formation in the absence and presence of carbonate have been observed during the ozonation of bromide-containing waters under standardized oxidant conditions.[56]

MODELING

Mechanistic Models. Kinetic models for the prediction of bromate formation during ozonation are set up by a combination of all of the relevant chemical equations with the corresponding rate constants in an equation system that may contain 100−200 reactions. Available codes such as Kintecus can be used to solve such coupled differential equations.[89]

Bromate modeling is one of the most challenging endeavors in environmental oxidation chemistry. The challenges are related to the roles of ozone and $^\bullet OH$ at various levels of the bromate formation pathway and also require modeling of the complex ozone chemistry in aquatic systems.

Kinetic Modeling of Ozone Decomposition. Even though rate constants for the inorganic reactions involved in ozone decomposition and the ensuing $^\bullet OH$ formation are available in the literature, there are two main challenges:

(i) Second-order rate constants for individual ozone decomposition reactions have been measured individually by different researchers, and large differences can be expected between different laboratories.[1] Therefore, ozone decomposition modeling has a high level of uncertainty.

(ii) The DOM can react with ozone and $^\bullet OH$ with second-order rate constants that vary from one type of DOM to another.[1,75] Furthermore, the fraction of promotion and inhibition of the radical chain reaction upon reaction of $^\bullet OH$ with DOM is not *a priori* known and has to be determined by fitting procedures.[76,90]

On the basis of these factors, ozone modeling in real waters has high levels of uncertainty. Several attempts to kinetically model ozone decomposition were made, but fitting of some of the rate constants was typically necessary to match the ozone evolution.[91,92] Transient $^\bullet OH$ formation was not even assessed in these models, and therefore, there is only limited application of such modeling exercises in real systems.

To overcome these inherent problems with ozone modeling, the experimentally determined ratios of the concentrations of $^\bullet OH$ and O_3 discussed above, R_{ct} has been applied to model bromate formation under well-defined conditions during ozonation and advanced oxidation with O_3/H_2O_2. This enabled a fitting of the second-order rate constant for the reaction of O_3 with $Br^\bullet$ ($k = 1.5 \times 10^8$ M^{-1} s^{-1}).[61]

Kinetic Modeling of Bromate Formation. Modeling of bromate formation was established first for ozonation systems in which $^\bullet OH$ radicals were scavenged. Such models can be set up with only a few kinetic equations and were successfully applied for a trend analysis of bromate formation for varying parameters in ultrapurified water.[18] If both O_3 and $^\bullet OH$ are included in such bromate formation models, >40 reactions are needed.[56,61,93] In addition, DOM may play an important role in quenching transient bromine species, such as HOBr and $Br^\bullet$.[47,66,72] Similar to the ozone decomposition models, this approach also has the inherent problem of second-order rate constants that were determined by different research groups. One case in point is the reaction of ozone with bromide, for which the two values in the literature differ by a factor of 1.6 [160 and 258 M^{-1} s^{-1} (see above)].[49,50] This example for a second-order rate constant that can be easily determined illustrates clearly the challenges of bromate formation models. Furthermore, if the >40 equations for bromate formation during ozonation of bromide-containing water are combined with the ozone decomposition chemistry, the level of uncertainty increases even more.

Nevertheless, kinetic bromate formation models can still yield useful information related to (i) relative bromate formation for changing water quality parameters (pH, ammonium, alkalinity, etc.), (ii) the contribution of a certain pathway to bromate formation, (iii) estimation of unknown rate constants for the reactions of transient bromine species with O_3 and $^\bullet OH$, and (iv) planning of tailored experiments to elucidate well-defined partial reaction systems. Bromate formation modeling has been extensively performed to support mechanistic studies for which relative changes in bromate are important and can be translated into mitigation strategies at full scale.[56,93]

Empirical Models. Since the early 1990s, nonmechanistic, empirical correlations have been applied to model bromate formation during ozonation of water and wastewater.[94,95] These can be generally categorized into three model types: linear regression, multilinear regression (MLR), and models based on artificial neural networks (ANNs).[26,96−106] Table S1 provides a list of various models, including their corresponding boundary conditions.

Applying real world data to several different models demonstrated a large variability, which is an inherent weakness of empirical models.[105] At their best, they were able to predict the trend of bromate formation with varying water quality parameters; however, the inaccuracy of the predicted bromate concentration was large. It appears that these models are highly water specific and should be used with caution, and not without prior model validation.

MITIGATION

Bromate control is challenging because of the need for micropollutant abatement and/or disinfection by ozone and/or $^\bullet OH$, which in turn leads to the formation of bromate. Several strategies can be applied before, during, or after ozonation to minimize the level of bromate in finished waters while maintaining the treatment goals (Figure 4). Strategies applied before or during ozonation aim to minimize the formation of bromate, whereas post-ozonation treatments focus on the abatement of bromate.

Bromate Minimization before Ozonation. Pretreatment strategies include processes located before ozonation aimed at bromide or DOC removal (Figure 4).

Bromide Removal. Electrochemical processes can remove ≤35% of bromide from natural waters in laboratory batch and continuous flow systems.[107,108] During the process, bromide is oxidized to bromine, which could potentially lead to formation of brominated compounds. Nevertheless, this may be offset by minimized brominated compound formation associated with lower bromide levels during oxidative post-treatment processes. Because bromate formation during ozonation is roughly proportional to the initial bromide concentration, this approach could partially mitigate bromate. However, for electrochemical

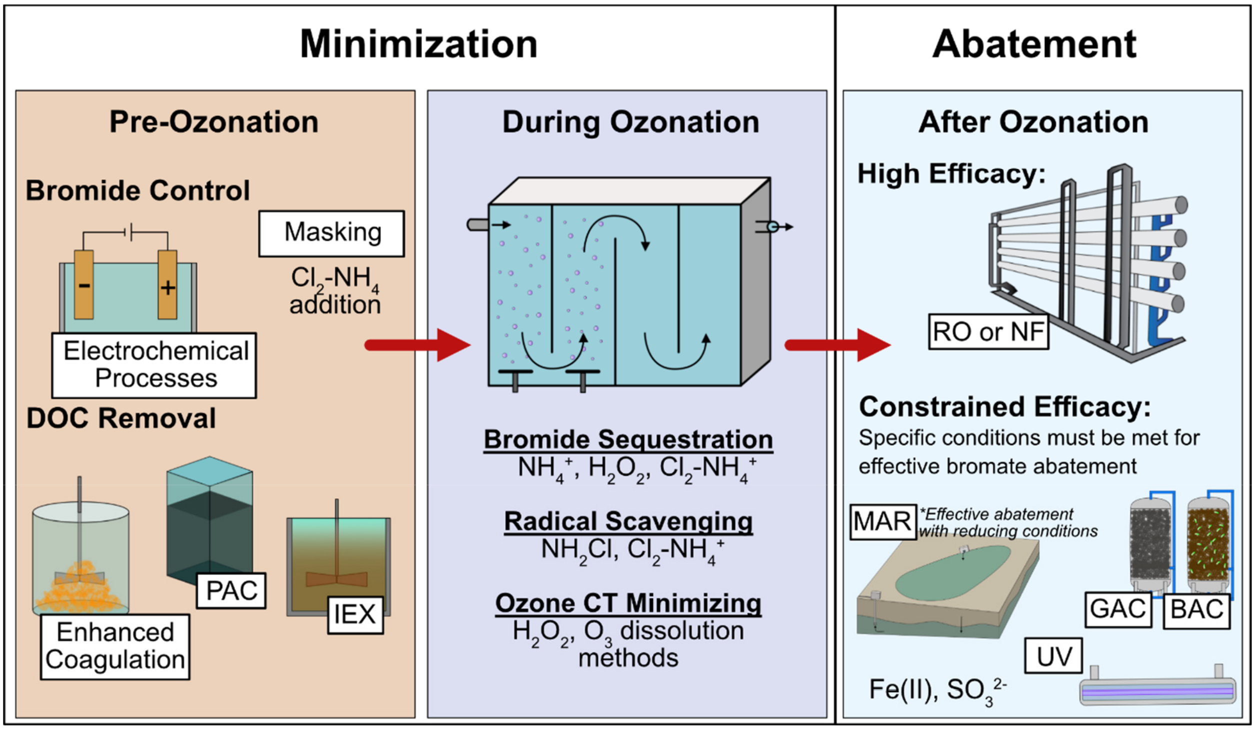

Figure 4. Overview of bromate mitigation strategies during pretreatment, ozonation, and post-treatment.

processes, up-scaling and cost/energy effectiveness lead to a limited applicability of this process in full-scale systems.[109]

A more promising bromide sequestration approach is the sequential addition of chlorine and NH_4^+,[110] and due to the multiple bromate suppression mechanisms that occur both before and during ozonation, it is described in greater detail in subsequent sections (see Ammonium- and Chloramine-Based Approaches).

DOC Removal. Treatments for DOC removal may inadvertently reduce bromate formation by decreasing the ozone demand to achieve target ozone exposures. This may be particularly relevant for waters with higher concentrations of DOC, such as wastewater.

Anion exchange resin has been demonstrated to remove ≤50−60% of bromide and DOC from natural waters.[111,112] Generally, bromate minimization occurred primarily from DOC rather than bromide removal.[113] During pilot-scale testing, magnetic ion exchange pretreatment removed 30% of the influent DOC and reduced the ozone dose requirements by 15−25% to meet CT requirements, which subsequently reduced the level of bromate formation by 35%.[114] Despite these promising results, this approach has not been readily implemented in full for bromate control.

Pretreatment by powdered activated carbon (PAC) can remove DOC. As a pretreatment step, it was shown to reduce the bromate yield at relatively large PAC doses (50−100 mg/L, >40% DOC removal), most likely due to the smaller doses of ozone needed to meet target micropollutant abatement.[95] However, for PAC doses in the range of 10−20 mg/L, an increased bromate yield was observed, potentially due to changes in electron-donating capacity of the DOM.[95] Because this behavior is not fully understood, more tests are needed before a broader application of this method will be possible.

DOC removal can also be achieved during enhanced coagulation, with optimal conditions based on coagulant type, pH, hydraulic conditions, etc.[115] In a study of three wastewaters, enhanced coagulation with 10−30 mg/L ferric chloride removed 10−47% of the DOC, which subsequently reduced the ozone dose by a similar percentage to meet treatment objectives.[116] This reduction in the applied ozone dose would likely reduce the level of bromate formation; however, further evaluation is necessary.

Bromate Minimization during Ozonation. There are several methods for minimizing bromate formation during ozonation, including reactor design and operation and chemical interventions (Table 1).

Process Design and Operation. Because reactor hydraulics should approach plug flow for efficient disinfection and oxidation, there is limited room for changes. However, one factor that can influence bromate formation is the ozone mass-transfer (i.e., dissolution of gaseous ozone in water) method and design.[117,118] There are two major methods for ozone mass transfer: (i) fine bubble diffusion (FBD) and (ii) addition of a concentrated ozone solution through a sidestream. Alternative ozone injection methods, such as injection through membranes or as micro/nanobubbles, have been developed, though their ability to minimize bromate formation has not yet been evaluated.

(i) In FBD systems, the first chamber of an ozone contactor is used for ozone gas−liquid transfer (Figure 5a). The ozone exposure (CT) in this dissolution zone (i.e., dissolution CT) is not included in regulatory disinfection credit (i.e., compliance CT). Therefore, the FBD chamber may contribute to bromate formation without any regulatory disinfection credit. When a treatment plant operates at design flow, the residence time in the FBD chamber can be minimized (often <2 min), which minimizes bromate formation in the ozone-transfer zone. However, during routine operation, flow rates can range from 25% to 60% of the design flow rate, resulting in longer contact times in

Table 1. Summary of Chemical Bromate Control Strategies

method	bromate minimization mechanism	bromate minimization efficiency	disinfection efficiency	oxidation efficiency	feasibility
pH depression	shifting HOBr/OBr$^-$ equilibrium, decreasing R_{ct} (increased O_3 stability)	pH 8 to 6 in drinking water, 50−91%[47,120]	enhanced (stabilized ozone)	potentially diminished for O_3 recalcitrant micropollutants (lower R_{ct})	expensive, requires storage of caustic chemicals, not applicable for medium/high-alkalinity water
NH_3 addition	HOBr quenching (NH_2Br formation)	42−73% (surface water, pH 8, 100−900 μg of NH_3-N/L)[47,120,123,124]	unaltered from conventional ozonation	unaltered from conventional ozonation	$^\bullet$OH pathway not affected, removal of excess ammonium in biological postfiltration
preformed NH_2Cl	decreasing R_{ct} (radical scavenging), HOBr and $Br^\bullet$ quenching	68−87% (wastewater, 1−5 mg of NH_2Cl as Cl_2/L)[129]	unaltered, although lower levels of ozone exposures have been demonstrated	potentially diminished for O_3 recalcitrant micropollutants (lower R_{ct})	monochloramine must be produced on site, removal of excess ammonium in biological postfiltration
chlorine−ammonium	bromide sequestration (NH_2Br formation), HOBr quenching	44−94% (surface water, 0.25−1.0 mg/L Cl_2 and 100−500 μg of NH_3-N/L)[123−125]	unaltered from ozone alone or slightly enhanced	unaltered from ozone alone	formation of chlorinated/brominated DBPs
H_2O_2	reduced lifetime of ozone, reaction with HOBr	−130% to 60% (surface water, 0.5−1.5 mol of H_2O_2/mol of O_3);[133] −50% to 67% (wastewater, 0.14−4.2 mol of H_2O_2/mol of O_3)[95,134,135]	diminished (low level of or no O_3 exposure)	enhanced (increased level of radical production)	residual H_2O_2 removal in biological postfiltration

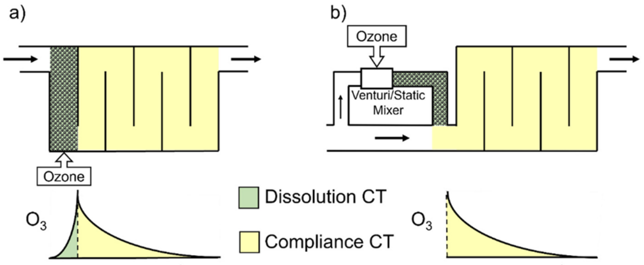

Figure 5. Comparisons of dissolution CT and compliance CT for different ozone mass-transfer systems: (a) conventional fine bubble diffuser and (b) sidestream addition.

the mass-transfer zone and thus higher levels of ozone exposure, leading to higher levels of bromate formation (2−7-fold in a pilot study).[117] Multiple contactor systems can take contactors out of service to minimize the residence time and the corresponding bromate production in the ozone mass-transfer zone.[117] This aspect of FBD should be considered when designing an ozonation process.

(ii) In sidestream systems, ozone gas is added to a sidestream water flow (10−20%) using venturi or static mixers and subsequently blended with the main water flow rate (80−90%) to achieve a target ozone dose entering the disinfection zone (Figure 5b),[82,117] which can minimize the dissolution zone CT compared to that of FBD systems. However, a nearly 5-fold larger ozone dose than in FBD is required in the sidestream to meet target dosages after blending. Hence, the residence time of the sidestream can influence the bromate concentration in the mainstream. Sidestream residence times increased bromate levels from 3−6 μg/L at 5 s to 40−140 μg/L at a residence time of >30 s.[117] Therefore, for the minimization of ozone decomposition and bromate formation, design guidance recommends that the residence time in the sidestream should not exceed 5 s, although time allowance for gas/liquid mass transfer should also be considered.[117]

pH Depression. Decreasing the pH influences both ozone stability and bromate formation (Table 1). A lower pH minimizes the amount of OBr^- available for oxidation by ozone (see Figure 2). However, because both HOBr and OBr^- are oxidized by $^\bullet$OH with similar second-order rate constants (eqs 13 and 14), another major benefit of a decrease in pH is increased ozone stability with a lower transient $^\bullet$OH concentration and a lower R_{ct}.[47] A decrease in pH from 8 to 6 typically results in a 50−60% decrease in the level of bromate formation in drinking water,[47,119] though a bromate minimization of >90% has also been demonstrated.[120] This approach allows for bromate minimization while meeting disinfection objectives. However, the chemical costs associated with pH depression, and subsequently increasing pH downstream, are in the range of 2−9 times higher than for ozone generation, depending on the water quality.[120] Because of this, pH depression is impractical for waters with moderate to high alkalinity, such as many drinking waters and wastewaters. Additionally, the decreased level of $^\bullet$OH generation caused by pH depression should also be considered, as it may be counterproductive to a desired oxidation of micropollutants.[95]

Ammonium- and Chloramine-Based Approaches. The literature refers to ammonium-based strategies as "ammonia"/

"NH_3" rather than "ammonium"/"NH_4^+". It should be noted that we are choosing to henceforth refer to these strategies as "ammonium", as this is the applied form. Ammonium addition suppresses bromate formation by forming monobromamine, NH_2Br, from hypobromous acid and ammonia ($k = 5.5{-}7.5 \times 10^7$ M^{-1} s^{-1}):[84,121]

$$HOBr + NH_3 \rightarrow NH_2Br + H_2O \tag{25}$$

preventing HOBr from being further oxidized to bromate. NH_2Br is oxidized by ozone to nitrate, releasing bromide again ($k = 40$ M^{-1} s^{-1}):[122]

$$NH_2Br + 3O_3 \rightarrow NO_3^- + Br^- + 3O_2 + 2H^+ \tag{26}$$

While the second-order rate constant for the reaction between hypobromous acid and ammonia is high, it should be noted that the reaction is between the two nonionic species. With pK_a values of 8.8 and 9.3 for $HOBr/OBr^-$ and NH_4^+/NH_3, respectively, neither can be the dominant species simultaneously. With the pH in the general range for drinking water or wastewater (6−8), the apparent second-order rate constant decrease by 1−2 orders of magnitude compared to the species specific second-order rate constant in eq 25.[121] While an increasing pH can increase the rate of NH_2Br formation, this leads to a lower ozone stability and potentially offsets the benefit of ammonium addition due to larger ozone doses required to meet disinfection objectives.[120] Regardless, in surface waters at pH ~8, the level of bromate was decreased by 40−73% (Table 1 and Table S2) across a wide range of ozone doses with ~200 μg of NH_4^+-N/L.[47,120,123,124] Because of the fast consumption of HOBr by ammonia, reaction 25 dominates the consumption of HOBr at 200 μg of NH_4^+-N/L ($k' = 28$ s^{-1}) over its further reaction with ozone ($k' \approx 3.2 \times 10^{-4}$ s^{-1} at 1 mg/L O_3) and $^\bullet$OH ($k' \approx 5 \times 10^{-4}$ s^{-1} for an R_{ct} of 10^{-8}) by orders of magnitude.

Bromate initiated by the oxidation of bromide with $^\bullet$OH is not efficiently mitigated by ammonium addition because HOBr is only a minor product of this pathway. Hence, the efficiency of ammonium addition for bromate mitigation depends strongly on the water characteristics and the importance of the main bromide oxidation pathway. This is also illustrated by the fact that bromate formation cannot be completely suppressed by ammonium addition, with often a maximum mitigation to 50−70%.[120,123] Because ammonium addition minimizes bromate through sequestration of bromine and not through the alteration of ozone and/or $^\bullet$OH exposure, the efficiency of ozone for either disinfection or oxidation is not affected (Table 1).

The chlorine−ammonium process was developed to provide enhanced bromate control beyond what is possible with ammonium addition alone.[119,124,125] In this process, chlorine is added upstream of ozonation to oxidize bromide to HOBr ($k = 1550$ M^{-1} s^{-1}):

$$HOCl + Br^- \rightarrow HOBr + Cl^- \tag{27}$$

Five to seven minutes of chlorine contact before ammonium addition is typical, though contact times as short as 1 min have been investigated.[119,124,125] Ammonium is then added to form NH_2Br prior to ozonation (reaction 25). Via the formation of NH_2Br prior to ozonation, the chlorine−ammonium process masks bromine and, in contrast to ammonium addition, can suppress bromate formation initiated by both O_3 and $^\bullet$OH. The level of bromate formation has been demonstrated to be reduced by 44−94%[119,123−125] depending on the treatment conditions (Table 1 and Table S3).

In addition to HOBr formation and quenching, the chlorine−ammonium process affects ozone performance in several ways. Preoxidation with chlorine decreases the ozone consumption rate and the level of $^\bullet$OH formation by altering the DOM.[125] This was also confirmed at pilot- and full-scale, where a decreased ozone demand and decay rate were observed, largely due to chlorine preoxidation, with a significantly increased level of ozone exposure at the same ozone dose.[124] Additionally, monochloramine is formed by the reaction of residual HOCl with NH_3. It is a weak $^\bullet$OH scavenger, which can partly suppress $^\bullet$OH reactions and stabilize dissolved ozone ($k = 5.2{-}5.7 \times 10^8$ M^{-1} s^{-1}):[126,127]

$$NH_2Cl + {}^\bullet OH \rightarrow NHCl^\bullet + H_2O \tag{28}$$

In one study, there was no difference in bromate formation for prechlorination contact times 1 or 5 min prior to ammonium addition. This is an indication that monochloramine alone may also play an important role in bromate suppression.[119]

On the basis of this observation, the options and limitations of NH_2Cl for bromate mitigation were investigated. To this end, it has been demonstrated that the ammonium−chlorine processes, in which mostly NH_2Cl is formed prior to ozonation, has a bromate mitigation effect similar to that of the chlorine−ammonium process. In this configuration, bromide will not be masked as bromamine prior to ozonation. Instead, bromochloramine can be formed during ozonation ($k = 2.86 \times 10^5$ M^{-1} s^{-1}):[128]

$$NH_2Cl + HOBr \rightarrow NHBrCl + H_2O \tag{29}$$

However, similar to the addition of ammonium, this does not quench the bromine radical pathway. In a comparative study, the ammonium−chlorine process reduced the level of bromate formation from 17 to 3−4 μg/L compared to a value of 2 μg/L for the chlorine−ammonium process.[119] Nevertheless, the ammonium−chlorine process was selected for bromate control because it resulted in a lower level of formation of trihalomethanes (THMs).

As a variant of the ammonium−chlorine process, preformed monochloramine has been added to wastewater to control bromate formation;[98] 5 mg/L NH_2Cl (as Cl_2) (~130 μM NH_2Cl) could reduce the level of bromate formation by ≤92%, depending on the specific ozone dose (Table 1 and Table S4). This dose is larger than what is commonly utilized in drinking water [1−2 mg of NH_2Cl/L (as Cl_2) (~15−30 μM NH_2Cl)]; however, the purpose of NH_2Cl addition is not disinfection of the distribution system but mitigation of bromate. Similar to ammonium addition, an optimum monochloramine concentration exists beyond which bromate minimization cannot be further enhanced.[81,125] Monochloramine minimizes bromate formation by several mechanisms: (i) quenching of $^\bullet$OH (see above), (ii) formation of bromochloramine, and (iii) quenching of $Br^\bullet$.

(i) As an $^\bullet$OH scavenger, monochloramine should stabilize ozone decay in drinking water. However, a certain increase in the ozone decay rate was observed in the presence of monochloramine both in river water and during water reuse.[129] This may be due to the reaction of monochloramine with ozone ($k = 26$ M^{-1} s^{-1}):[52]

$$NH_2Cl + O_3 \rightarrow NO_3^- + Cl^- + 2H^+ \tag{30}$$

The $^\bullet$OH scavenging of NH_2Cl not only mitigates bromate formation but also may reduce the rate of oxidation of ozone-resistant compounds, such as 1,4-dioxane.[129]

(ii) Even though the formation of bromochloramine from the reaction of NH_2Cl and Br^- is often mentioned as a mitigation effect for bromate, this is not very likely. The apparent second-order rate constant at circumneutral pH for the formation of bromochloramine from the reaction of NH_2Cl with Br^- is low ($k = 1.4 \times 10^{-1}$ M^{-1} s^{-1}):[130]

$$NH_2Cl + Br^- \rightarrow \text{products} \tag{31}$$

For a NH_2Cl concentration of 5 mg/L as Cl_2 (~130 μM NH_2Cl), an ozone concentration of 1 mg/L, and an R_{ct} of 10^{-8}, the fractions of Br^- reacting with NH_2Cl, O_3, and $^{\bullet}OH$ are 0.3%, 94%, and 5.7%, respectively. This shows clearly that reaction 31 is not an efficient sink for bromide.

(iii) It has been shown that $Br^{\bullet}$ reacts with a k of 4.4×10^9 M^{-1} s^{-1} with NH_2Cl.[67] An addition of 15 μM NH_2Cl (~1 mg/L as Cl_2) can reduce the contribution of the O_3−$Br^{\bullet}$ reaction (eq 18) from 8−15% to 2−4%, and therefore, the NH_2Cl−$Br^{\bullet}$ and NH_2Cl−HOBr reactions contribute roughly equally to the reduction of the level of bromate formation.[67]

Hydrogen Peroxide. The addition of hydrogen peroxide (H_2O_2) during ozonation leads to an advanced oxidation process (AOP), which can maintain micropollutant abatement and mitigate bromate formation compared to conventional ozonation with the same ozone dose.[61,95]

Ozone reacts only with HO_2^- (eq 32), which is present in only a minor fraction at neutral pH ($pK_{a,H_2O_2} = 11.6$).[131] The reaction of O_3 with HO_2^- ($k = 5.5 \times 10^6$ M^{-1} s^{-1}; $k_{app,pH7} = 140$ M^{-1} s^{-1}) produces $^{\bullet}OH$ with a yield of ~50% through a complex mechanism, which is discussed elsewhere (eq 32).[1,55,131]

$$O_3 + HO_2^- \rightarrow \rightarrow 0.5{}^{\bullet}OH \tag{32}$$

O_3/H_2O_2 can influence bromate formation on two levels: (i) reduction of the lifetime of ozone and (ii) quenching of HOBr.[132]

(i) Enhanced transformation of O_3 to $^{\bullet}OH$ in the O_3/H_2O_2 process results in a shift toward the formation of $Br^{\bullet}$ (eqs 9 and 10). Under these conditions, $Br^{\bullet}$ will primarily react with DOM back to bromide (eq 19) due to the resulting shorter lifetime and lower transient concentration of O_3.

(ii) Reduction of HOBr by H_2O_2 ($k = 7.6 \times 10^8$ M^{-1} s^{-1}) proceeds by eq 33:[62]

$$HOBr + HO_2^- \rightarrow Br^- + H_2O + O_2 \tag{33}$$

with an apparent second-order rate constant of ~2×10^4 M^{-1} s^{-1} at pH 7. For a H_2O_2 concentration of 1 mg/L, the half-life of HOBr is ~1 s at pH 7.

The performance of H_2O_2 for bromate suppression is quite variable (Table 1 and Table S5); an 85% decrease and a 110% increase in the level of bromate formation have been reported in bench testing and in full-scale systems relative to conventional ozonation.[95,133−135] These differences are largely due to different operational conditions, with either constant ozone doses or constant ozone residual, for conventional ozonation and the O_3/H_2O_2 process, respectively, although the water matrix can also impact the efficacy of H_2O_2.[135] If a constant ozone dose is applied for the two processes, the level of ozone exposure decreases in the O_3/H_2O_2 process and therefore the level of bromate formation decreases. For a constant ozone residual, the ozone exposures for the two processes are similar, while in the O_3/H_2O_2 process, the level of $^{\bullet}OH$ exposure increases, which leads to a higher level of bromate formation. Therefore, O_3/H_2O_2 should not be used for treatment objectives that include disinfection of bacteria and protozoa due to the necessity to maintain an ozone residual. A significant inactivation of viruses can still be with the O_3/H_2O_2 process, despite there being no measurable CT.[136] This is caused by the high second-order rate constants for virus inactivation with ozone.[81,137]

Several novel approaches to ozone contactor design have been developed to maximize $^{\bullet}OH$ exposure while minimizing bromate formation in the presence of H_2O_2 by multiple smaller doses (for more details, see section S.1 of the Supporting Information).[109,132,138,139] A serial O_3/H_2O_2/LP UV process approach allowed for application of optimized ozone doses and demonstrated minimal bromate formation while achieving significant abatement of micropollutants.[140]

Alternative Chemical Control Strategies. Preoxidation processes with various oxidants, such as chlorine, chlorine dioxide, and permanganate, may affect ozone and $^{\bullet}OH$ chemistry, and thus potentially bromate formation, through changes in DOM properties. Typically, this leads to a higher ozone stability and allows the partial mitigation of bromate formation, while a certain disinfection target can be reached.[124,141] Heterogenous catalytic ozonation in which a catalyst, such as metal oxides (e.g., FeOOH), is added to enhance ozone transformation to $^{\bullet}OH$[142] have been demonstrated to reduce the level of bromate formation by ≤91%.[143] However, there are numerous issues related to heterogeneous processes and large doses of catalysts are required, which have prevented full-scale applications so far.[109] In a preliminary study, a very low level of bromate formation with effective abatement of micropollutants was achieved by ozonation in the activated sludge reactor instead of the clarified secondary effluent.[144]

Post-Treatment for Bromate Abatement. Abatement of bromate downstream of ozone treatment has largely proven to be unsuccessful, with the exception of high-pressure membrane treatment such as reverse osmosis (RO) and nanofiltration (NF). It has been demonstrated that 96−97% of bromate can be removed in pilot- and full-scale RO systems after ozonation,[145,146] whereas NF membranes have been demonstrated to remove 45−77% with rejection increasing at high pH and ionic strength and decreasing in the presence of DOM.[147] This is especially relevant in the context of wastewater reuse that typically has DOC concentrations higher than those of natural waters. However, RO and NF may not be viable options or cost-effective for some systems (i.e., inland communities) employing upstream ozone, but RO and NF could be particularly useful for an integrated process train with multiple water quality goals, if both ozone and RO are necessary for potential regulatory requirements (e.g., California's Draft Criteria for Direct Potable Reuse).[148] Other post-ozone treatment processes have demonstrated limited success in the abatement of bromate, such as granular activated carbon and biofiltration,[149−161] ion exchange,[162−168] managed aquifer recharge,[169−174] ferrous iron and sulfite,[175−178] and UV irradiation.[179−181]

PRACTICAL CONSIDERATIONS

A one-size-fits-all approach to bromate mitigation is difficult to achieve. Absolute bromate concentrations will depend on both the water matrix composition, including bromide levels, and treatment goals. Only once bromate levels are demonstrated with a particular water and particular treatment conditions can a

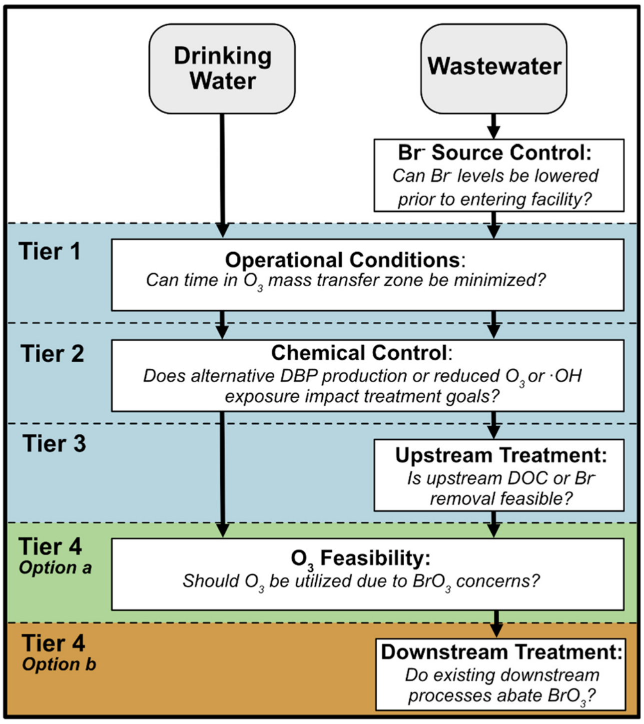

Figure 6. Tiered approach for the assessment of bromate control strategies based on the results of this work. In the blue area, the focus should primarily be on removing bromide from entering the ozonation process and on minimizing bromate formation through optimizing ozone dissolution, adding specific chemicals that sequester bromide, and/or disrupting bromate formation reactions. In the green area, if these solutions are not viable, then the question of whether ozone should be used should be assessed. The brown area shows options and limitations of downstream treatment for bromate abatement.

mitigation strategy be chosen for application. An approach for making such decisions is suggested in Figure 6. Outside of approaches that can be taken by the utility, an additional option worth mentioning is bromide source control. In the case in which there is a known bromide point source, elimination via diverting this waste stream, or eliminating bromide via treatment prior to discharge, could lead to reduced bromide levels entering the treatment facility and thus a reduced level of bromate formation.[22] This approach is not feasible for most drinking water utilities but could be considered, if necessary, for wastewater treatment facilities.

Tier One. Ideally, operational conditions affecting the extent of ozone transfer versus regulatory CT should first be considered, for both drinking water and wastewater treatment approaches. The ozone exposure should be minimized in portions of the contactor where no ozone CT credit is measured or assigned. This can be achieved by the selection (e.g., FBD and SSI) and optimization of the dissolution method (e.g., distributed ozone diffusion and reduction of sidestream residence time), which can reduce the level of bromate formation and overall cost.

Tier Two. If bromate levels are still increased after the optimization of operational conditions, a chemical control during ozonation should be considered. The chemical strategy of choice should be based on the specific treatment objectives for the ozone process, as many of the chemical strategies can affect ozone and $^{\bullet}$OH exposures. In these cases, practitioners are often challenged with balancing treatment goals with bromate formation. For instance, if ozone is implemented for disinfection purposes, it is not appropriate to utilize hydrogen peroxide as a bromate control strategy as it greatly reduces the level of ozone exposure (CT). However, this strategy would still allow for micropollutant oxidation. Furthermore, addition of chloramine or hydrogen peroxide may require the management of residuals during downstream treatment processes, such as biofiltration. Table 1 provides an overview of the different chemical addition strategies.

Tier Three. If bromate levels are still an issue, then upstream treatment minimizing either bromide or DOC, such as enhanced coagulation or PAC, could be considered. However, on the basis of the inconclusive results for different DOC removal options, such an approach should be used with caution. Preliminary bench- or pilot-scale testing with the specific source water and specific upstream treatment should be evaluated to demonstrate the extent, if any, of bromate mitigation. Such upstream treatments, if successful, also have the added benefit of reducing the size of the ozone doses necessary to achieve treatment goals, particularly in wastewater. This could potentially lower overall ozone costs, although this analysis is outside the scope of this work. DOC removal is less relevant for drinking water treatment due to the lower DOC levels compared to those of wastewater.

Tier Four. A majority of post-ozonation bromate abatement strategies are generally ineffective; therefore, relying on such an approach for bromate mitigation is not recommended. A universal promising approach to the abatement of bromate appears to be RO; however, it is cost-prohibitive if it is not already utilized for other treatment objectives and is not typically realistic for drinking water treatment facilities. The lack of post-ozonation bromate abatement options highlights the necessity of focusing efforts on minimizing bromate formation during ozonation. However, abstaining from an ozone-based process altogether may be the most feasible option for a challenging matrix. In these cases, alternate treatment processes may be desirable depending on the treatment objectives. For example, If disinfection and micropollutant abatement are desired, the AOP UV/H_2O_2 system may be an option,[60,109] whereas if treatment is solely targeting micropollutant abatement, activated carbon (GAC, PAC, etc.) could be utilized.[182,183]

RESEARCH NEEDS

This Critical Review has highlighted several current research needs, which are particularly important considering the continued interest in using ozone for drinking water treatment or enhanced wastewater treatment for potable reuse, irrigation, or ecosystem protection:

- Better mechanistic understanding of the mitigation strategies based on chlorine and ammonia, including remeasurement of some of the second-order rate constants.
- Better mechanistic understanding of bromate mitigation during heterogeneous ozonation in the presence of metal oxides.
- Further development of analytical methods for online determination of bromate concentrations to adapt treatment for changing water qualities.
- Process optimization to better control the balance between treatment objectives and bromate formation (i.e., multiple-point peroxide addition, multistage mass transfer, and novel ozone-transfer systems).

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- Standardized reporting of ozone and $^{\bullet}$OH exposures during bromate control studies, including determination methods. This would allow a better evaluation of the trade-offs between bromate control and other treatment objectives (i.e., oxidation and/or disinfection).
- Further evaluations of the ability of upstream treatments that aim to remove DOC to minimize bromate formation during ozonation. Certain upstream treatments, such as enhanced coagulation, may allow for several water quality changes that can impact bromate formation, such as DOC concentration, pH, and alkalinity reduction.
- Determinations for the need to manage chemical residuals, i.e., chloramine and hydrogen peroxide, for downstream treatment processes, such as biofiltration.
- Field demonstration for the reduction of the level of bromate in managed aquifer recharge systems for potable reuse applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c00538.

> Details on $Br^{\bullet}/Br_2^{\bullet-}$ concentrations as a function of bromide; summary of bromate formation models; and water quality data demonstrating the performance of ammonium, chlorine−ammonia, preformed monochloramine, and hydrogen peroxide for bromate control (PDF)

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Notes

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