Effect of several natural water constituents on bromate formation during ozonation

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Abstract Synthetic water matrices containing ammonia, bicarbonate, hydrogen peroxide, and natural organic matter were studied to identify the effects of these compounds (individually and in combination) on bromate formation. Ammonia alone was observed to significantly reduce bromate formation through the sequestering of brominated intermediates as bromamines. Natural organic matter reacted quickly with bromamines, which could impair the ability of ammonia to block bromate formation. Bicarbonate was observed to generally promote bromate formation in otherwise pure water, but bicarbonate worked synergistically with ammonia to reduce bromate formation by a greater factor than ammonia alone, due to OH radical scavenging. Experiments showed that hydrogen peroxide lowered the effectiveness of ammonia to block bromate formation.

Keywords Ammonia; bicarbonate; bromamines; bromate, by-products; ozone

Introduction

Drinking water that is treated with ozone for disinfection often contains bromate from the reaction between ambient bromide and both ozone and hydroxyl radicals. Health concerns associated with long-term exposure to low levels of bromate (Kurokawa *et al*. 1986) have led to its regulation in many parts of the world, with limits typically in the 10–25 µg/L range (e.g. Health Canada 2000; US-EPA 1998).

There has been considerable research conducted to establish the mechanisms and characteristics of bromate formation in ozonated water. This research has investigated primarily bromate formation in otherwise pure water (e.g. Von Gunten and Hoigné, 1994), or else has investigated the effects of natural water constituents one at a time (e.g. Song 1996). It was the goal of the research reported in this paper to confirm some of the earlier reported impacts of natural water constituents on bromate formation both alone, and in combination.

Objectives

- To investigate the effect of ammonia (alone) on bromate formation.
- To investigate the effect of (bi)carbonate alkalinity (alone) on bromate formation.
- To investigate the joint effect of ammonia and (bi)carbonate alkalinity on bromate formation.
- To explore the potential for natural organic matter to affect the ability of ammonia to block bromate formation, either by reaction with bromamine intermediates, or formation of hydrogen peroxide.

Methods and materials

Experiments were conducted in 2 L semi-batch reactors using pure water (Milli-Q®) spiked with known concentrations of desired compounds. In the semi-batch reactors, a fixed volume of water was normally ozonated continuously at a rate equal to the rate of ozone loss, allowing for a steady ozone concentration to be maintained (±5%). The water was always

prepared with 2 mM phosphate buffer to maintain an approximately fixed pH (± 0.2 units). It is known that phosphate reacts with hydroxyl radicals, however, the rate is slow enough to be safely ignored under the experimental conditions. (Bi)carbonate alkalinity was added using reagent grade $NaHCO_3$ and Na_2CO_3. Hydrogen peroxide (H_2O_2) was applied as a 30% solution. For all H_2O_2 experiments, 60 mg/L of (bi)carbonate alkalinity (as $CaCO_3$) was added to provide a baseline condition. pH was adjusted immediately prior to the experiments using HCl or NaOH. The water was then ozonated for about 15 minutes to obtain the desired ozone concentration, at which point ammonia (NH_4Cl), bromide (KBr), and H_2O_2 were added to begin the experiment.

The natural organic matter (NOM) applied to the water matrix was prepared by adding 130 mg of Suwannee River NOM, purchased from the International Humic Substances Society, to 240 mL of Milli-Q® water. The resulting solution was then passed through a 0.45 µm Teflon® filter. The final total organic carbon was measured to be 210 mg/L as carbon, and was used as a stock solution.

Ozone was produced using a Hankin OzoTitan® generator (Scarborough, Canada) and pure oxygen. Aqueous ozone was measured spectrophotometrically using direct absorbance at 258 nm ($\varepsilon = 2{,}950$ $M^{-1}cm^{-1}$) (*Standard Methods for the Examination of Water and Wastewater*, 1992). This method was first calibrated against the indigo method to ensure accuracy and precision. Bromate and bromide measurements were made using a Dionex DX-500 ion chromatograph equipped with a high capacity column (Dionex, 1997). Residual ozone in the samples was quenched using a fivefold stoichiometric excess of ethylenediamine (EDA).

Results and discussion

Effect of ammonia alone

The impact of ammonia on bromate formation has been studied quite thoroughly in the past (e.g. Hofmann and Andrews, 2000). Bromate can be modeled as being formed through three pathways, called the Direct (D), Indirect/Direct (I/D) and Direct/Indirect (D/I) pathways, according to the sequence in which bromide is first oxidized, either directly by ozone, or indirectly by the hydroxyl radical ($OH^\bullet$) (Figure 1). When ammonia is present, it reacts with the free bromine ($HOBr/OBr^-$) that is formed as an initial step in the D/I and D pathways to form bromamines (NH_2Br, $NHBr_2$), much as free chlorine reacts with ammonia to form chloramines. Bromamines do not form bromate, and so ammonia is predicted to be able to effectively block these two pathways. In theory, it will not block the I/D pathway, and so ammonia would be predicted to slow, but not completely stop, bromate formation.

Experiments supported this theory, as shown by the data in Figure 2. In the first 10 minutes of ozonation, bromate formed approximately four times more slowly in the presence of ammonia than without ammonia. However, ozone was observed to slowly oxidize the ammonia to nitrate, and once the ammonia was gone, bromate formation resumed at a much higher rate.

An important consideration is the amount of ammonia required to block the D and D/I
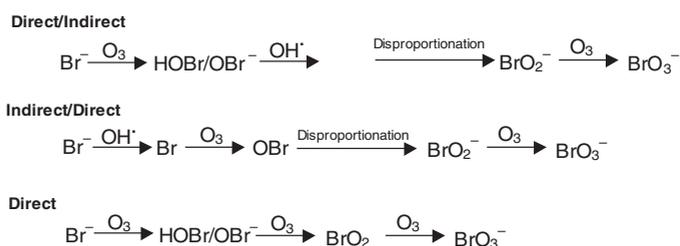
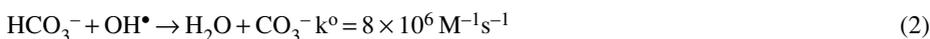**Figure 1** Simplified bromate formation pathways, as reported by Song (1996)
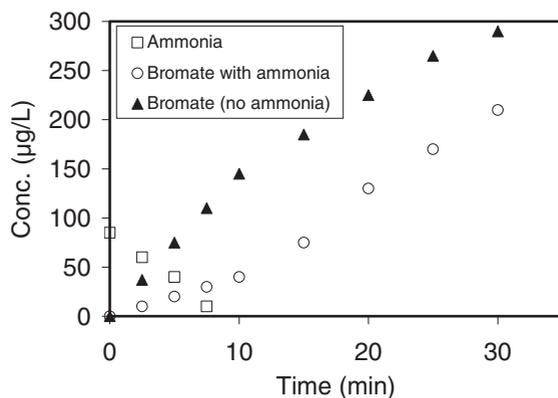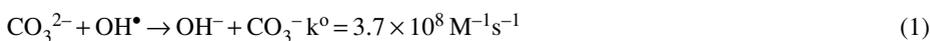
Figure 2 Measured bromate formation in the presence and absence of ammonia, and ammonia depletion ($O_3 = 2\,mg/L$, pH 7.5, $Br^- = 0.2\,mg/L$, NH_4^+-N $= 0.1\,mg/L$, 20°C).

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pathways. Experiments showed that molar ammonia:bromide ratios of greater than 3:1 provided little additional benefit in terms of reducing the rate of bromate formation (data not shown). Of course, greater starting concentrations of ammonia prolonged the period of time that bromate formation was suppressed until the ammonia was completely oxidized, as occurred after approximately 10 minutes in Figure 2.

### Effect of (bi)carbonate alkalinity alone

(Bi)carbonate alkalinity has been reported in the past to have conflicting impacts on bromate formation. This may be due to its effect, not only bromate formation chemistry, but also on ozone stability. (Bi)carbonate scavenges $OH^\bullet$ according to the following reactions (Buxton *et al.*, 1988):

$$CO_3^{2-} + OH^\bullet \rightarrow OH^- + CO_3^- \quad k^o = 3.7 \times 10^8\,M^{-1}s^{-1} \tag{1}$$

$$HCO_3^- + OH^\bullet \rightarrow H_2O + CO_3^- \quad k^o = 8 \times 10^6\,M^{-1}s^{-1} \tag{2}$$

This has several conflicting consequences. Hydroxyl radicals are required in two of the three bromate formation pathways (Figure 1), so by scavenging the $OH^\bullet$, (bi)carbonate should slow down bromate formation. However, $OH^\bullet$ accelerates ozone decomposition, so ozone will be more stable in water containing (bi)carbonate, thereby prolonging the time available to form bromate. Furthermore, the carbonate radicals formed in Reactions 1 and 2 can themselves promote bromate formation via a different pathway (Song, 1996). These conflicting influences of (bi)carbonate have never been studied under controlled conditions.

Experiments were conducted in which the bromate concentrations in water with different levels of (bi)carbonate were recorded following 15 minutes of ozonation. Ozone was delivered two ways: either with a constant concentration of 2 mg/L over the 15 minutes, or with an initial dose of 2 mg/L which was allowed to decay over the 15 minutes. The results are shown in Figure 3.

It was hypothesized that in the scenario where ozone was allowed to decay, an increase in (bi)carbonate would stabilize the ozone with the result that more bromate would be formed. The data support this hypothesis as shown by the open triangles in Figure 3. In the case of a constant ozone concentration of 2 mg/L, it was hypothesized that an increase in (bi)carbonate concentration would lead to a reduction in bromate formation due to inhibition of the D/I and I/D pathways (Figure 1). This was not observed (Figure 3). In fact, there

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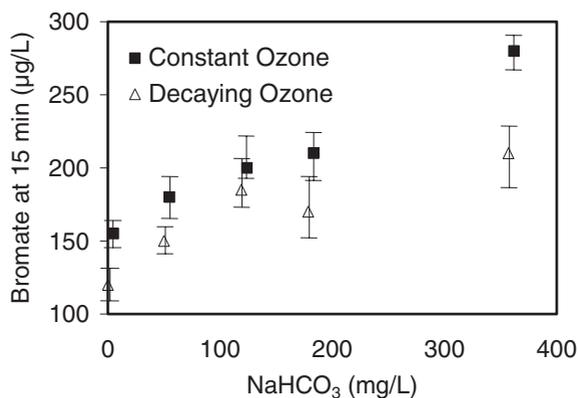
Figure 3 Impact of (bi)carbonate on bromate formation (2 mg/L ozone, constant or decaying). Error bars give the range of four replicates, pH 7,5, 0.2 mg/L Br⁻, 20°C

was a significant increase in bromate formation with increasing (bi)carbonate concentration. No information is currently available to confidently propose a theory to explain this observation, however such an explanation would require that the carbonate radicals that are formed via Reactions 1 and 2 be more effective than $OH^\bullet$ in producing bromate. It is known that $OH^\bullet$ is an extremely indiscriminate reagent. It is possible that the $OH^\bullet$ could be reacting with impurities in the Milli-Q® water (whose total organic carbon is approximately 0.05 mg/L, for example), while the carbonate radical may be more prone to targeting only compounds leading to bromate. The one-to-one "substitution" of $OH^\bullet$ for carbonate radicals may therefore promote bromate formation under these conditions. The next step will be to examine whether such an impact is observed in natural water matrices.

Combined effect of ammonia and (bi)carbonate

In theory, ammonia can block the D and D/I pathways of bromate formation (Figure 1). The remaining I/D pathway requires $OH^\bullet$ to proceed. This raises the intriguing possibility that ammonia and (bi)carbonate can act together to inhibit all three pathways, with the (bi)carbonate scavenging the $OH^\bullet$ required by the I/D pathway.

An experiment was conducted to test this hypothesis, with water containing excess ammonia ozonated with increasing levels of bicarbonate. The results shown in Figure 4 support the hypothesis, with less bromate formed with greater (bi)carbonate concentrations
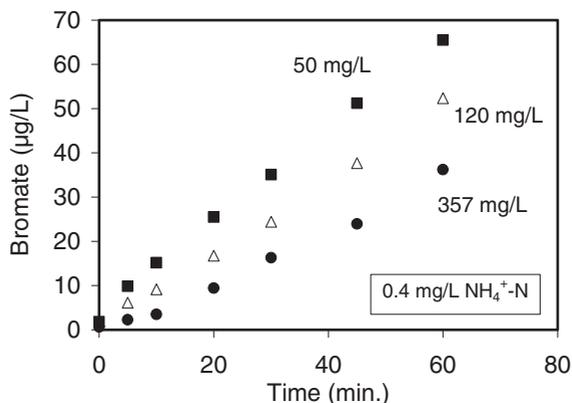
Figure 4 Effect of inorganic carbon (mg/L as $CaCO_3$) on bromate formation in the presence of ammonia (2 mg/L O_3, 0.2 mg/L Br⁻, pH 7,5, 20°C)

in combination with ammonia. It must be cautioned, however, that this result was observed in otherwise pure water. In natural waters containing organic matter, the interaction between the organics and the OH• might lead to different results than shown here. Further research is underway.

Combined effect of ammonia and hydrogen peroxide

If ammonia is capable of inhibiting the D and D/I bromate formation pathways but not the I/D pathway, it implies that H_2O_2 would accelerate bromate formation in water where ammonia is present. This is because H_2O_2 reacts with ozone to form OH•, needed in the one pathway that ammonia does not inhibit. H_2O_2 may be produced when ozone reacts with natural organic matter (NOM), and so is likely to be common at low concentrations during ozonation.

An experiment was conducted to test the hypothesis that H_2O_2 would accelerate bromate formation in the presence of ammonia (Figure 5). As predicted, the rate of bromate formation increased rapidly when H_2O_2 was applied. The H_2O_2 also caused the O_3 concentration to drop, as it reacted with the O_3 to form OH•. Once the H_2O_2 had completely reacted with the ozone (after about 12 minutes in Figure 5) the rate of bromate formation decreased to its initial level. These results suggest that ammonia would be less effective at inhibiting bromate formation in waters where OH• concentrations are higher, as would be the case if a particular NOM were susceptible to H_2O_2 formation.

Reaction between bromamines and natural organic matter

NOM can be expected to affect bromate formation a number of ways, the most obvious being scavenging of the $HOBr/OBr^-$ intermediates (resulting in organobromine formation), reacting with OH•, the formation of H_2O_2, and exerting an ozone demand. A previously unreported yet potentially significant impact of NOM on bromate formation in natural waters might also be the ability of NOM to destroy the bromamine intermediates that sequester bromine from the bromate formation pathway in waters containing ammonia or organic amines (which would likely include most surface waters).

An exploratory experiment was conducted to investigate the reactivity of monobromamine with a model NOM under baseline conditions. A 1 μM solution of monobromamine (a typical concentration during ozonation) was applied to a 1 mg/L solution of NOM at pH 7.5. The monobromamine concentration was then monitored over time. The results shown in Figure 6 indicate that monobromamine reacts quickly with NOM, with an apparent half-life of the order of minutes. The half-life in pure water, in contrast, would be expected to be in the order of hours (Hofmann and Andrews, 2001). If the reaction between
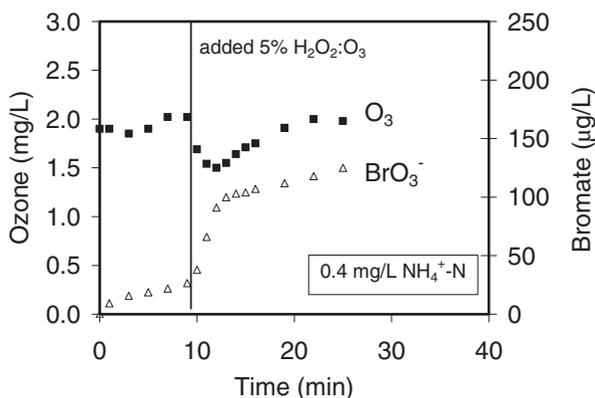
Figure 5 Effect of H_2O_2 on bromate formation in the presence of ammonia
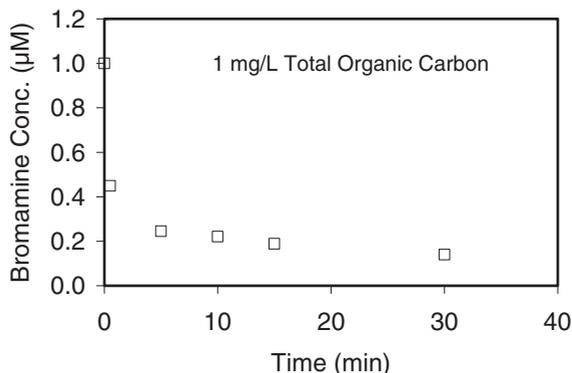
Figure 6 Decomposition of monoromamine in the presence of NOM

NOM and monobromamine were to yield bromide and nitrate or nitrogen gas, as is the case in the equivalent reaction between NOM and chloramines, then this reaction would impair the ability of ammonia to block the D and D/I bromate formation pathways since ammonia would be removed while bromide was being returned to the bromate formation pathway (Figure 1). This could help to explain why several studies have reported ammonia to be less effective at inhibiting bromate formation in practice than is observed in the laboratory using synthetic waters with low organic carbon concentrations (e.g. Coffey *et al.*, 1999).

Summary

Natural waters contain many constituents that may interact in their effect on bromate formation. This research and other studies have demonstrated that ammonia at concentrations typical in natural waters (e.g. 0.05 mg/L-N) is theoretically capable of blocking two out of three bromate formation pathways. The simultaneous presence of (bi)carbonate may provide additional benefit by scavenging the $OH^\bullet$ required in the third pathway. In contrast, hydrogen peroxide formed via the reaction between NOM and O_3 can promote this third pathway and render ammonia less effective.

The role of NOM is complex. Apart from serving as a source of H_2O_2, it may directly scavenge certain bromate intermediates, consume ozone, promote $OH^\bullet$ formation or, as observed in this study, react with bromamines. This latter phenomenon may be a significant factor in studies using natural waters that found ammonia to be less effective at inhibiting bromate formation than would be predicted in experiments using otherwise pure water.

The impact of (bi)carbonate is also complex, being able to both inhibit and promote bromate formation through different mechanisms. In this research, the promoting mechanisms appeared to dominate in the (synthetic and otherwise pure) water matrices studied.

It should be cautioned that all of this research was conducted in laboratory-prepared water, and the results may not accurately extrapolate to water matrices containing other compounds (such as different types of NOM). Work is underway to study the same phenomena in natural waters.

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