

ROLE OF HYDROXYL RADICALS AND HYPOBROMOUS ACID REACTIONS ON
BROMATE FORMATION DURING OZONATION

by

Peng-Fei Chao

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Peng-Fei Chao

has been approved

October 2002

APPROVED:

, Chair

Supervisory Committee

ACCEPTED:

Department Chair

Dean, Graduate College

ABSTRACT

Ozonation of waters containing bromide ions (Br^-) results in Br^- oxidation by ozone and its decomposition by-product (*e.g.*, hydroxyl radical (HO^\bullet)) to form different intermediate brominated species (*e.g.*, hypobromous acid (HOBr), hypobromite ions (OBr^-), bromite (BrO_2^-), bromide radicals (Br^\bullet), and hypobromite radicals (BrO^\bullet)) and eventually to form bromate (BrO_3^-), a suspected carcinogen. In this study, bench- and pilot-scale experiments were conducted with Colorado River Water (CRW) to investigate the kinetics and control of bromate formation.

Bromate formation is strongly influenced by water quality and treatment variables. Some water quality parameters (*e.g.*, bromide level, pH, temperature and (bi)carbonate alkalinity) have positive effects on bromate formation, while the presence of natural organic matter (NOM) and ammonia reduce the amount of bromate formed. Increasing ozone dose and/or contact time increases bromate formation. Quantification of bromate formation is expressed by the R_{CT} value, the ratio of HO^\bullet exposure (or concentration) to ozone exposure (or concentration). Two phases of R_{CT} are performed and the values of R_{CT} remain unchanged throughout the ozonation process with a set of water quality. The R_{CT} values for ozonation of CRW water range between 10^{-7} and 10^{-9} , resulting in HO^\bullet concentrations of on the order of 10^{-12} to 10^{-14} M.

Bromate formation can be controlled by adding acid or ammonia to decrease intermediate OBr^- . Acid addition to lower water pH from ambient (8.2) to 7.5 and 6.5 reduces bromate formation by 30% and 80%, respectively. In comparison, adding ammonia reduces bromate formation up to 60% and 85% at pH 7.5 and 8.5, respectively. Ammonia's efficiency to mitigate bromate formation is lessened with lowered water pH. Bromate formation by HO^\bullet radical pathways cannot be controlled unless radicals are being scavenged. Inorganic carbonate species can scavenge HO^\bullet and form carbonate radicals that react with OBr^- to form bromate.

The reaction rate of chlorine or bromine with NOM is rapid and dependent upon NOM characteristics. Bromination is approximately one order of magnitude faster than chlorination. The slower NOM reaction sites have a rate constant of approximately $50\text{ M}^{-1}\text{s}^{-1}$, which is 3 to 4 orders of magnitude less than the fast NOM reaction sites. Pre-ozonation reduces the NOM reactivity by approximately 50%. Kinetically, the impact of bromate reduction by the reaction of intermediate HOBr and NOM is only important during the fast ozonation stage ($t < 2$ minutes). A negligible impact on bromate reduction by HOBr and NOM reactions at slow ozonation stage ($t > 2$ minutes) can be implied based upon the rate constants and reactivity of NOM.

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4. CHAPTER 1

5. INTRODUCTION

5.1. 1.1 INTRODUCTION

Ozone was first recognized as a disinfectant for polluted water in 1886 by de Meritens (Vosmaer, 1916). A few years later an ozonation pilot plant was constructed to test ozone's application for the disinfection of drinking water in Germany, and the results showed that ozone was very effective for the disinfection of bacteria (Vosmaer, 1916). Until the 1970's, ozonation became increasingly popular as a technology for drinking water disinfection in Europe. The perception of ozonation as a "clean" oxidation process with fewer harmful disinfection byproducts (DBPs) than chlorination has also led to a rapid interest by American municipalities in the past decade.

Ozone provides several advantages over conventional chlorine water treatment. Lin and Yeh (1993) stated that ozone was much safer to use than chlorine (ozone is made on site at low pressure and it is easy to stop its production). Interest in the use of ozone has been increasing steadily, primarily as the results of both health concerns associates with the formation of disinfection by products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), which form upon chlorine addition. Ozonation is currently considered one of the most effective microbial disinfection technologies (Finch et al., 1994). Ozone provides other water treatment benefits over chlorine, since it is a stronger oxidant. In water treatment ozone and its decomposition oxidant by-products, hydroxyl radicals (HO^\bullet), can effectively control taste and odor causing compounds such as geosmin and methylisobroneol (MIB) (Lalezary, 1986; Glaze et al. 1990), remove color imparted by humic substances (Flogstad and Odegaard, 1985), oxidize ferrous and manganese (Stoebner and Rollag, 1981) and, most importantly, inactivate certain microorganisms such as *Ciardia lamblia* cysts and *Cryptosporidium* oocysts (Sobsey, 1989) for which chlorine is less effective. However, ozone has some drawbacks, such as forming inorganic and organic by-products when added during water treatment for disinfection purposes. Najm and Krasner (1995) identified a total of 15 organic and inorganic DBPs including bromate, bromoform, debromoacetonitrile (DBAN), brominated HAAs, CNBr, ketoacides and aldehydes. The major drawback during ozonation is that bromide can be easily oxidized to bromate (von Gunten and Hoigne, 1993; Siddiqui and Amy, 1993), a

possible human carcinogen, even in waters containing trace amounts of bromide. As a result, the United States Environmental Protection Agency has regulated the maximum contaminant levels of bromate at 10 µg/L by the Stage I Disinfectants/Disinfection By-Products Rule (USEPA, 1998). Considering a national average bromide level of between 80 and 100 µg/L (Amy, 1994), typical water ozonations could lead to a violation of the proposed BrO₃⁻ MCL. Recent studies have shown that bromate formation is due to a combination of bromide oxidation by molecular ozone and its decomposition by-product, HO[•], in ozonated waters containing bromide. The overall (chain) reactions of these oxidation processes are very complex and some oxidized intermediate aqueous bromine species are formed, which include hypobromous acid (HOBr) and hypobromite ion (OBr⁻) (Haag and Hoigne, 1983; Westerhoff, 1995), bromide radicals (Br[•]) and hypobromide radicals (BrO[•]) (von Gunten and Hoigne, 1994). The rate of bromate formation and contribution by either ozone and/or HO[•] are dependent upon the water quality characteristics and ozone treatment variables (Song, et al., 1996). Water quality characteristics, such as pH, natural organic matter (NOM) source and concentration, temperature and (bi)carbonate alkalinity strongly affect the reaction mechanism, therefore changing the distribution of bromine species as well as bromate formation. On the other hand, different ozone application such as ozone dose, contact time or water and/or gas flow rates can significantly affect bromate formation. In ozonation water treatment processes, different ozone doses and reaction times, pH adjustment, ammonia addition and/or hydrogen peroxide addition are usually applied in order to balance disinfection efficiency and bromate formation, and therefore, make the overall reaction chemistry even more complicated. Thus in order to evaluate advantages and risks of ozonation processes, it is necessary to gain a full knowledge of the overall reaction mechanism and kinetics, considering all factors, before one can design adequate bromate control strategies that maximize disinfection efficiency. To approach this purpose, kinetic data are needed to predict what products will remain in the water after specified durations of ozonation. In addition, kinetic data are also important for learning more about the environmental behavior of ozone when introduced into natural aquatic systems. The Colorado River water (CRW) was selected as a representative of natural water since it is a major water supply for the four six southwestern states, and many water treatment plants using CRW are, or will be, practicing ozonation.

Although the mechanisms and kinetics of bromate formation have been well investigated and models that predicting bromate formation during ozonation have been developed, most studies had not

thoroughly considered DOC and ammonia effects in natural waters. These two factors could be quite important on affecting bromate formation under various water qualities (e.g., different pH, (bi)carbonate alkalinity and NOM concentration and characteristics). Therefore, the goal of this study is to contribute to the better understanding of bromate formation by focusing on three key issues, which are lacking from previous studies:

- 1) Effects of HO[•] concentrations and ratio of oxidant pathways (O₃/ HO[•]) on bromate formation in natural waters.
- 2) Effects of aqueous bromine scavenging by ammonia on bromate formation.
- 3) Effects of aqueous bromine scavenging by NOM on bromate formation.

The research plan has been designed to address issues related to bromate formation, but the results will also be beneficial to the broader scientific community as well. It will be of interest to researchers studying both ozonation DPBs and chlorination DPBs. It could provide useful information for determining the reaction rates of O₃ with NOM, calculating the HO radical concentrations present during ozonation and understanding the formation and stability of organic by-product such as aldehydes. More importantly, it could provide strategies such as ammonia addition and/or pH depression for balancing DBP formation against microbial protection under a wide range of conditions.

5.2. 1.2 DESCRIPTION CHAPTERS

The description of this dissertation includes the following sections, which address the four hypotheses and research objectives.

- Chapter 2: Literature Review provides a review of the relevant archival studies on the ozone chemistry, mechanisms of the inorganic DBP bromate formation as well as reactivity of organic DBP formation by halogenation. This is basic information that is needed to understand the subsequent chapters
- Chapter 3: Research Objectives and Research Hypotheses state the research goal of this study and present the development of the four research hypotheses that accompany a rational discussion of relevant background on each hypothesis. Each of the hypotheses is described below:

Hypothesis I: Bromate formation increases proportionally to the ratio of $[HO^\bullet]/[O_3]$ during ozonation, affected by different water qualities (pH, DOC, temperature, ammonia and (bi)carbonate alkalinity) and water treatment conditions (ozone dose, contact time and flow rate).

Hypothesis II: HO^\bullet concentrations decrease proportionally with increasing DOC and (bi)carbonate alkalinity and decreasing pH in natural waters.

Hypothesis III: Ammonia addition for controlling bromate formation does not alter the $[HO^\bullet]/[O_3]$ ratio, but shifts bromate formation towards the HO^\bullet oxidation pathway by scavenging HOBr/Br⁻.

Hypothesis IV: Aqueous bromine reacts faster with NOM than aqueous chlorine. The rate of reaction between bromine and chlorine with NOM is affected by the characteristic of NOM and pH.

- Chapter 4: provides a general review on the effects of ozone decomposition and HO^\bullet production kinetics by water quality characteristics and treatment variables. In addition, the Hypothesis II is addressed in this chapter.
- Chapter 5: examines the effects of ozone and hydroxyl radicals on bromate formation during ozonation process. This chapter addresses Hypothesis I and supports the co-relationship between bromate formation and R_{CT} , which are affected by water quality characteristics and treatment variables.
- Chapter 6: investigates the control of bromate formation by ammonia and address the Hypothesis III.
- Chapter 7: determines the reactivity and disinfection by-product formation of aqueous chlorine and bromine with natural organic matter. The Hypothesis IV is addresses in this chapter.
- Chapter 8: provides the summary and conclusions of the overall research.

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6. CHAPTER 2

7. LITERATURE REVIEW

This chapter summarizes the background information of disinfection by-product formation in ozonation and halogenation (chlorination/bromination). The first part describes the current understanding of ozonation on bromate formation as well as source of bromide and parameters that affect the formation of bromate. The second part depicts the chemistry background of aqueous chlorine and bromine. In addition, kinetics and mechanism of aqueous chlorine or bromine reaction with NOM will be discussed.

7.1. 2.1 OZONATION

7.1.1. 2.1.1 Ozonation Concerns

Ozone is a disinfectant and oxidant commonly used in the United States and Europe to treat drinking water (Langlasis, et al., 1991). It is an advanced treatment process for disinfection, oxidation of metals, oxidation of organics, removal of taste and odor, removal of THM precursors and increasing biodegradability of organics before GAC filtration (Langlais et al., 1991). However, the present of trace bromide in water has become a problem of major concern through: (1) the recent observation of bromine formation during ozonation of waters containing bromide (Kuo, et al., 1990; Krasner, et al., 1993; Siddiqui and Amy, 1993), (2) the publication of World Health Organization (WHO) temporary guidelines on bromate, and (3) the formation of undesirable brominated organic by-products (Glaze, et al., 1993 and Song, et al., 1996). In 1993, bromate was included in the drinking water guidelines of the WHO. WHO proposed a minimum level of 25 µg/L, which corresponds to a 7×10^{-5} excess risk level, based on risk assessment of a 10^{-5} risk level of 3 µg/L (WHO, 1993). The USEPA introduced a MCL for bromate of 10 µg/L based on the considerations of minimal health risk, current available treatment technologies, and limitation of laboratorial detection. The same value was proposed by the drinking water commission of the European Union.

7.1.2. 2.1.2 Source of Bromide

Geological formations are the major natural source of bromide in ground waters, while the discharge of saline water is the main source of anthropogenic pollution of surface water. Bromide occurs in nearly every drinking water source at concentrations ranging from less than 10 µg/L to nearly 3,000 µg/L (Krasner et al., 1989). In a study of 101 US drinking water sources, Amy et al. (1994) found a national average bromide level ranging between 80 and 100 µg/L. During ozonation, the formation of bromate occurs when source water contains bromide (Siddiqui et al., 1995). Since the guideline for bromate as proposed by the WHO is very low, bromate formation has brought considerable worldwide attention in all water treatment facilities that use ozone.

7.1.3. 2.1.3 Mechanism and Pathways of Bromate Formation

Bromate formation is via a series of oxidation processes in waters containing bromide. When ozone is applied as a disinfectant, ozone may either react directly with dissolved species or decompose to form secondary oxidants such as HO radicals, which may then lead to a series of radical chain reactions accompanied by further ozone consumption. Von Gunten and Hoigne (1994) introduced a model including a molecular ozone pathway and a HO[•] pathway for bromate formation. Figure 2.1 shows possible reactions for molecular ozone mechanism and the HO[•] pathway (shown by dashed line). Details of each pathway will be discussed as follows:

Among these pathways, HO[•] leads to the formation of BrO[•] through several pathways, followed by undergoing a disproportionation to hypobromite and bromite:

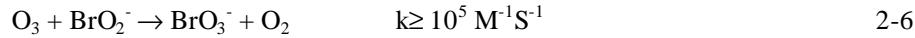
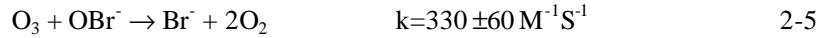
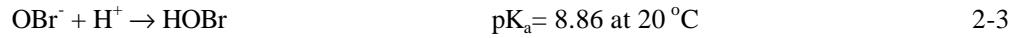
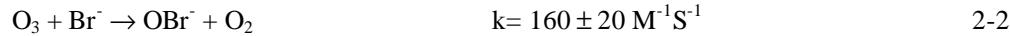


Bromate is then formed through the oxidation of bromite and hypobromite by ozone. The HO[•] mechanism for the formation of bromate thus includes two decisive reaction steps, which are still associated with molecular ozone.

Based on von Gunten and Hoigne's developed model, Song et al (1996) proposed that major bromate formations in ozonation are via three major pathways (Figure 2.2), which were defined as direct ozonation, direct-indirect ozonation combination and indirect-direct ozonation combination pathways. The

first pathway is the direct ozonation pathway, represented by the following reaction mechanism (Haag and Hoigne, 1983):

Direct ozonation pathway:

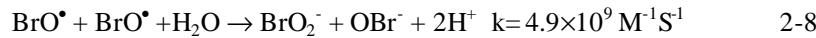
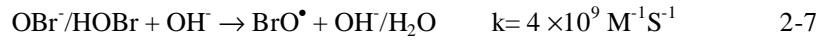


The overall reactions show that ozone sequentially oxidizes Br^- to aqueous bromine (HOBr/OBr^-), and then BrO_3^- . Since OBr^- rather than HOBr can be oxidized to bromite at a highly appreciable rate, BrO_3^- formation is favored at high pH upon continuous ozonation.

The second pathway for bromate formation follows OBr^- formation via direct ozonation of Br^- (Eqn. 2-2 and 2-3); HO^\bullet oxidizes OBr^- to bromate rather than molecular ozone (Amy, et al., 1995).

Overall, this second mechanism can be combined with Equations 2-2 and 2-3 plus the following reactions:

Molecular ozone initiation/ HO^\bullet radical combination pathway:



Bromite can be oxidized to bromate through either direct ozonation (Eqn 2-6) or indirect ozonation (Equation 2-9 through 2-11) in which it is oxidized by HO^\bullet to BrO_2^\bullet which disproportionates to bromate. Based on the analysis of competition kinetics, bromite oxidation to bromate is predominated through the direct ozonation pathway (Song et al., 1996).

The final bromate formation mechanism is based upon HO^\bullet initiating bromide oxidation through the formation of Br^\bullet . The bromine atom is further oxidized by molecular ozone to form BrO^\bullet , which continues to form bromate through Equations 2-8 to 2-11 and Equation 2-6 (Yate and Stenstrom, 1993; von Gunten and Hoigne, 1994). This overall reaction pathway can be represented by the following reactions:

HO[•] radical initiation/molecular ozone combination pathway:



where the rate constant of reaction between ozone and bromide radical was estimated by analogous gas phase reactions and kinetic modeling.

The importance of each pathway contributing to bromate formation depends on raw water quality characteristics and water treatment processes (Song et al., 1996). In addition, during advanced oxidation processes (AOP) with ozone and hydrogen peroxide (H_2O_2), H_2O_2 addition would decrease molecular ozone concentration in favor of HO^{\bullet} radical concentrations. Low molecular ozone concentrations limit OBr^- / HOBr formation while high HO^{\bullet} concentrations increase the importance of the combination pathway of HO^{\bullet} initiation and molecular ozone for bromate formation. Moreover, hydrogen peroxide kinetically outcompetes O_3 or HO^{\bullet} for OBr^- or HOBr , thereby eliminating any dependence upon aqueous bromite as a major intermediate in bromate formation; the rapid reaction between hydrogen peroxide and hypobromite is given as follows (von Gunten and Oliveras, 1995):



7.1.4. 2.1.4 Parameters Affecting Bromate Formation

Bromate formation during ozonation in waters containing bromide is a function of the following parameters:

- Ozone dose
- Initial bromide concentration
- NOM characteristic and concentration
- pH
- Temperature
- (Bi)carbonate alkalinity
- Ammonia.

All the above factors could affect rates of ozone decomposition and HO[•] generation and concentrations, thus affecting the kinetics of bromate formation and relative amounts of bromate formed. In addition, they can also directly affect bromate formation by influencing the species and concentration of HOBr/OBr⁻.

Many researchers have studied the extents of effect on bromate formation by the above parameters. Results from batch experiments indicate that bromate formation was favored at high values of pH, initial bromide concentration, (bi)carbonate alkalinity, temperature, and ozone dose. On the other hand, increasing dissolved organic carbon and ammonia concentration decreased bromate formation. Table 2.1 lists general effects and reasons of bromate formation and TOBr formation by the parameters in ozonation, although some exceptions are noted in the literature.

Based upon an orthogonal experimental design examining the influence water quality characteristics and treatment variables, Song et al. (1996) developed an empirical bromate formation model from observed batch ozonation data at 20°C:

$$[\text{BrO}_3^-] = 10^{-6.11} [\text{Br}]_o^{0.88} [\text{DOC}]^{-1.18} [\text{NH}_3\text{-N}]^{-0.18} [\text{O}_3]^{\text{dose}^{1.42}} \text{pH}^{5.11} [\text{IC}]^{0.18} (t)^{0.27} \quad 2-16$$

The following order of importance was observed based upon the results used to obtain this bromate formation model:

Increase bromate formation: pH > O₃ > Br⁻ > IC

Decreasing bromate formation: DOC > NH₃-N

All effect on bromate formation: pH > O₃ > DOC > Br⁻ > NH₃-N ≡ IC

7.1.5. 2.1.5 Development of Ozonation Kinetic Models

In order to make adequate predictions for disinfection, oxidation and bromate formation during the ozonation process and therefore to design adequate bromate control strategies that maximize disinfection efficiency, accurate predictive models for bromate formation are desired. Most predictive models are empirical models (Westerhoff and Ozekin, 1997; Ozekin and Amy, 1997; Siddiqui and Amy, 1993), but these models have limited flexibility and could not be widely applied. Although mechanistic-based

numerical models for bromate formation have been developed, they can only predict bromate formation in DOC-free waters (Haag and Hoigne, 1985; von Gunten and Hoigne, 1994; Westerhoff et al., 1998a).

There are several advantages of mechanistic-based models over empirical models. For example, empirical models have limited flexibility; they are only suitable for predicting bromate concentrations for the conditions to which they were calibrated (e.g., bromide concentrations above 100 µg/L or high ozone dosages). Mechanistic based models could be applicable to a wider range of conditions. Mechanistic-based models are also flexible and additional reaction components (e.g., hydrogen peroxide reactions) can easily be incorporated to simulate new bromate control strategies (e.g., alcohol addition to scavenge HO radicals) (Westerhoff, 1998). Therefore, if mechanistic-based numerical models can be developed and calibrated to include DOC and ammonia-related reactions, then they would prove to be much more robust than empirical models.

7.1.6. 2.1.6 Ozone Decomposition

The knowledge of ozone decomposition kinetics is essential in terms of model development. In the ozonation process, the mechanism and kinetics of ozone decay and the formation of HO[•] provide important information on bromate formation. Understanding the ozone decomposition process is the first step in order to determine the formation of bromate in waters containing bromide.

Ozone decomposition kinetics has been studied for decays. Langlais et al. (1991) summarized two most acceptable ozone decomposition mechanisms for drinking water conditions, which based upon work by Hoigne, Staehelin, and Bader (HSB model) and work by Gordon, Tomiyasu, and Fukutomi (GTF model). Both models describe ozone decomposition as a series of chain reaction, which are initiated by hydroxide ion and the overall ozone decomposition reactions by first-order kinetics, which are pH dependent (Chelkowska et al., 1992).

Based on experimental observation, Hoigne and coworkers (1982) concluded that in the pure water the decomposition of ozone is initiated by its reaction with the hydroxide ion, resulting in the following rate:

$$-\frac{d[O_3]}{dt} = k[O_3][OH^-]$$

2-17

Tomiyasu et al. (1985) empirically fit the following equation to their data:

$$-\frac{d[O_3]}{dt} = k_1[O_3][OH^-] + k_2[O_3]^2[OH^-]$$

2-18

The value of k_{OH^-} and k_2 vary markedly with solution composition (i.e. ozone and OH⁻, the presence or absences of scavengers such as CO₃²⁻, PO₄³⁻, etc). However, the second term could be canceled if the pH of water is decreased or sufficient amount of radical scavengers is present. The mixed order rate expression is thus reduced to that of Hoigne et al's approach shown in Eqn. 2-17.

In natural waters, the chemistry of ozone becomes ever more complicated. In dealing with the ozonation of organics in natural water, it is difficult to establish which of the two primary pathways dominate, although it appears that the radical pathway is most likely dominate in the oxidation (Singer, 1990). Because of the interaction of multiple mechanisms, the empirical kinetics describing the rate of ozone depletion deduced by different researchers disagree even with respect to the order of reaction (Grasso and Weber, 1989). Staehelin and Hoigne (1985) proposed a reaction scheme to describe the interaction of organic solutes with the radical chain reaction (Figure 2.3). The significant features of the scheme include: 1) the radical pathway of ozone decomposition consist of initiation, propagation and termination steps; 2) the presence of inorganic and organic matter could initiate promote and prohibit the radical chain reaction; 3) O₂[•] radical is highly selective, thereby predominately catalyzing the decomposition of ozone molecules; 4) HO[•] react with ions present before they react with other radical species. Therefore, the overall kinetic equation is quite complex. Considering that it is impossible to quantify all dissolved species in water and their associated reactivity with ozone, Yurteri and Gurol (1988) offered a simplified scheme to obtain an expression for dissolved ozone consumption in natural waters:

$$-\frac{d[O_3]}{dt} = w[O_3]$$

2-19

$$\log w = Bo + a(pH) + b\{\log(TOC) - c[\log(alkalinity/10)]\}$$

2-20

where w is the specific ozone utilization rate, and Bo, a, b, and c are empirical coefficients. However, recent evidence has shown that the specific ozone utilization rate w is not constant as ozonation proceeds. It appears that the ozone consumption occurs in at least two stages: a very rapid immediate ozone decomposition stage, followed by a much slow rate process (Guittonneau et al., 1992). It was therefore suggested that a rate expression for dissolved ozone in natural waters must account for changes in water composition during the course of ozonation.

7.1.7. 2.1.7 Modeling for Bromate Formation Prediction

According to van Gunten and Hoigne (1994), in the presence of an organic scavenger for HO[•], bromate formation can be precisely predicted by the molecular ozone mechanism. However, in the absence of scavengers, HO[•] reactions contribute significant to bromate production. Therefore a model needs to account for both O₃ and HO[•] oxidation reactions (Figure 2.4). A mathematical model predicting the formation of bromate has been developed by Siddiqui et al (1994). The model takes into account pH, DOC, ozone and bromide concentrations and temperature. However, the model makes no allowance for ammonia and/or radical scavenger contribution to bromate formation.

In this study the bromate formation module includes reactions for the oxidation of bromide to bromine and bromate. The model accounts for both O₃ and HO[•] oxidation reactions. The kinetic parameters can then be incorporated into a system of differential equation, providing a mathematical description of mechanism that can predict bromate formation. It will use oxidation reactions presented in Table 2.2, 2.3 (von Gunten, 1994) and 2.4 (Westerhoff, 1998), from which the basis of existing bromate formation programs were developed. The existing model will be expanded to include reactions between both aqueous bromine and bromide radicals (BrO[•]) and NOM. The developed model will be capable of predicting time-dependent concentrations of bromate during ozonation of water containing NOM.

Once the kinetic model is developed, it will allow users to accurately predict bromate formation during ozonation of natural waters containing bromide. In addition, it will give a good insight into the complex mechanism of bromate formation chemistry. Moreover, it could be used to verify existing and identify unknown chemical reaction pathways and the impact of bromate control options, such as the addition of ammonia and pH depression.

7.1.8. 2.1.8 Bromate Control

Application of ozone to treat potable water has its limitations. Although ozone provides a number of benefits in terms of water treatment, bromate formation is the major health concerns. Balancing between ozone disinfection/oxidation benefits and adverse bromate formation impact is very challenging.

A number of possible methods to control formation of bromate during ozonation have been proposed including (1) reduction of initial water bromide levels, (2) scavenging HO radicals (HO[•]) in

which formed as ozone decomposition by-products that can oxidize bromide to bromate, (3) lowering intermediate hypobromite ions (OBr^-) during ozonation, and (4) removal of bromate after ozonation. Attempts to physically or chemically reduce bromate's precursor, bromide ion, existing in waters tend to be impractical and efforts to remove once formed bromate from ozonated water could be cost ineffective or impractical (Asami et al., 1999; Amy et al., 1997). Therefore, the focus of treatment strategies should be on preventing the formation of bromate.

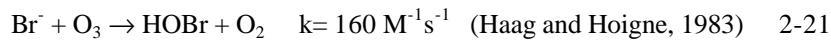
In drinking water treatment, the reduction of intermediate OBr^- concentration by decreasing water pH and/or addition of ammonia is probably the most applicable option in controlling bromate formation (Pinkernell and von Gunten, 2001). However, the method of pH depression to control bromate formation might cause corrosion problems, and for waters with high (bi)carbonate alkalinity, adding large amounts of acid to control bromate formation below the MCL might not be economical. On the other hand, it has been demonstrated that the presence of ammonia can reduce bromate formation during ozonation processes (Haag et al., 1984; Hoigne et al., 1993; Song et al., 1997; Hofmann and Andrews, 2001; Pinkernell and von Gunten, 2001). Recent studies conducted by several researchers (Hofmann and Andrews, 2001; Pinkernell and von Gunten, 2001) showed that even a small amount of ammonia led to significant reduction of bromate compared to waters without ammonia during ozonation.

Recently, the Information Collection Rule (ICR) regulated by the EPA that proposed all public water systems (PWSs) which use surface or groundwater under the direct influence of surface water and serve more than 100,000 persons, and PWSs which use only ground water and serve more than 50,000 persons shall conduct treatment study to monitor their water quality. Results of bromide and ammonia concentrations from 467 nationwide treatment facilities from July 1997 to December 1998 are shown in Figure 2.4 and 2.5, respectively (TWGDAW, 2002). It is observed that almost all water sources contain bromide and approximately 40% of the treatment plant influents exceed bromide concentration of 50 $\mu\text{g/L}$. Thus, bromate formation must be concerned when applying ozone into the treatment process. On the other hand, ammonia is also detected in nearly every drinking water source. Figure 2.5 shows that over 70% of the treatment plant influents exceed the ammonia concentration of 100 $\mu\text{g/L}$. Therefore, some water sources may already perform bromate reduction potential.

7.2. 2.2 HALOGENATION (CHLORINATION/BROMINATION)

Disinfection by-products (DBPs) form during ozonation or chlorination of waters containing natural organic matter (NOM) as well as bromide ions (Br^-), which both exist ubiquitously in drinking water sources (Minear and Amy, 1996). The formation mechanisms of chlorination by-products have been extensively investigated since humic substances were first identified as precursors for trihalomethanes (THMs) in natural water disinfection processes (Rook, 1974). On the other hand, the increasing use of ozone in water disinfection processes has brought considerable concern in regards to the inorganic DBP formation of bromate in waters containing bromide. Considering the public health risk from these toxic compounds, EPA has regulated the maximum contaminant levels (MCL) of THMs to 80 $\mu\text{g/L}$ and HAAs to 60 $\mu\text{g/L}$ for water treatment utilities using chlorination process and 10 $\mu\text{g/L}$ for bromate for those using ozonation process. In order to achieve these stringent regulations by performing adequate treatment strategies, chemistry of chlorine and bromine in regards to their reaction with aqueous NOM must be, first of all, well defined.

In both ozonation and chlorination of waters containing bromide, bromide can be initially oxidized to form aqueous free bromine (expressed as HOBr for summation of HOBr and OBr^-). The reactions are as follows:



During ozonation process, the highly reactive intermediate bromine formed from oxidation of bromide will continue to be oxidized by both ozone and its decomposition by-product, HO^\bullet , to bromate. Meanwhile, a portion of this intermediate bromine will react with NOM and form organo-bromine compounds. During chlorination process, on the other hand, bromine as well as chlorine tends to react with NOM and form organo-bromine and -chlorine by-products. This shows that both bromine-NOM interactions in ozonation and bromine-NOM and chlorine-NOM interactions in chlorination play very important roles in controlling the formation of bromate or halogenated DPBs in water

treatment. It has been observed that organo-bromine compounds (e.g., CHBr_3) are formed more rapidly than organo-chlorine compounds (e.g., CHCl_3) during chlorination. However, most of the literature available on the formation mechanisms of halogenated compounds was developed by adding chlorine to waters in the presence of Br^- . Further investigation on the respective reactivity of NOM with aqueous chlorine as well as aqueous bromine is needed to better understand individual reaction mechanism, and thus provide improved insight into the development of more effective control measures for better DBP formation during drinking water treatment operation.

7.2.1. 2.2.1 Hydrolysis of aqueous Chlorine or Bromine

When free chlorine or bromine (chlorine/bromine) reacts with water, a special type of oxidation-reduction reaction occurs. The chlorine/bromine hydrolysis reaction is also a disproportionation reaction yielding HOCl/HOBr with $\text{Cl}^{(+I)}/\text{Br}^{(+I)}$ ion and HCl/HBr with $\text{Cl}^{(-I)}/\text{Br}^{(-I)}$ ion. The pKa for chlorine, with equal coexistence of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), is 7.6 (Morris, 1966) and is 8.8 for bromine, with equal coexistence of hypobromous acid (HOBr) and hypobromite ion (OBr^-) (Haag and Hoigne, 1983; Westerhoff, 1995) at 20 °C. When oxidation of a substance by chlorine/bromine occurs, the $\text{Cl}^{(+I)}/\text{Br}^{(+I)}$ in HOCl/HOBr gains two electrons oxidizing to $\text{Cl}^{(-I)}/\text{Br}^{(-I)}$ ion.

7.2.2. 2.2.2 Kinetics and Mechanisms of Chlorine/Bromine with NOM

Early kinetic studies of the chlorination of phenol and chlorine-substituted phenols by Soper and Smith (1926) and later by Lee (1967) have shown that the overall reaction is second-order and proportional to the concentration of aqueous chlorine and

phenol at pH greater than 6. It is anticipated that NOM reactivity towards aqueous bromine or chlorine is related to its characteristics. However, unlike a single organic compound, which has specific physically and chemical properties, NOM contains a heterogeneous mixture of organic compounds with quite different structures and characteristics varying as a function of hydrogeology and biogeochemistry within watersheds. Therefore, it is expected that the reactivity between chlorine/bromine would vary with different NOM sources.

A conceptual approach was proposed by Song et al. (1996) for determining rate constants between aqueous chlorine/bromine species and NOM. Using aqueous bromine reactions with NOM as an example, the reactions between hypobromous acid and hypobromite ion with a model organic compound can be expressed as follows:



where ϕ is the number of moles of M reacting with either bromine specie, M_{oxid} is the product of bromine oxidation of M, M_{sub} is the product of bromine substitution with M and bromide (Br^-) is a by-product from formation. The above reactions are overall second-order reactions. Since we cannot determine the product formations of M_{oxid} and M_{sub} , it could be assumed the reactions are pseudo-first order with respect to bromine concentration in the presence of excess NOM. Second-order rate constants of HOBr and OBr⁻ can then be determined. The experimental approach will determine the rate constants between HOBr/OBr⁻ and NOM.

Ultraviolet absorbances in the range of 250 to 280 nm (UV₂₅₄₋₂₈₀) and ¹³C-NMR have been used commonly to characterize NOM (Rostad et al., 2000; Reckhow et al., 1990). In addition, specific ultraviolet absorbance at wavelength 254 nm

(SUVA=UV₂₅₄/DOC), a surrogate for aromatic carbon, has often been correlated with DBP formation (Edzwald et al., 1985; Reckhow et al., 1990; Larson and Weber, 1994; Najm et al., 1994; Korshin et al., 1997; Croue et al., 1999). Reckhow et al. (1990) conducted chlorine oxidation studies with several purified hydrophobic organic acids of NOM from several different sources and found out a significant correlation between aromatic, phenolic, and activated aromatic properties of the NOM fraction and chlorine demand. By following the same basic principles for the reactivity of chlorine with NOM, Symons et al. (1993) found that bromine reacts with organic matter faster and more effectively than does chlorine.

By applying these technologies to characterize halogenated organic compounds can, therefore, determine the respective reactivity of NOM with aqueous chlorine as well as aqueous bromine. Furthermore, it will also provide insight of the reaction mechanisms (e.g. oxidation and substitution) controlled by differences of physical and chemical properties between chlorine and bromine.

7.3. REFERENCES

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Table 2.1 - Effects and reasons of bromate and TOBr formation in ozonation.

Parameter	pH ↑	O ₃ ↑	Temp ↑	Alk. ↑	H ₂ O ₂ ↑	NH ₃ ↑	Br ⁻ ↑
Effects	TOBr ↓	TOBr ↑↓	TOBr ↑	TOBr ↓	TOBr ↓	TOBr ↓	TOBr ↑
	BrO ₃ ⁻ ↑	BrO ₃ ⁻ ↑	BrO ₃ ⁻ ↓	BrO ₃ ⁻ ↑	BrO ₃ ⁻ ↑	BrO ₃ ⁻ ↓	BrO ₃ ⁻ ↑
Reasons	HOBr/ OBr ⁻	Oxidant level	Activation Energy	HCO ₃ ⁻ / CO ₃ ²⁻	Oxidants	NH ₃ consume bromine	Initial Br ⁻ level

Table 2.2- Reaction and rate constants for molecular ozone mechanism (von Gunten and Hoigne, 1994)

Equation Number	Reaction	k or pK _a	Reference
1	Br ⁻ + O ₃ → BrO ⁻ + O ₂	160 M ⁻¹ s ⁻¹	Haag and Hoigne, 1983
2	BrO ⁻ + O ₃ → Br ⁻ + 2O ₂	330 M ⁻¹ s ⁻¹	Haag and Hoigne, 1983
3	BrO ⁻ + O ₃ → BrO ₂ ⁻ + O ₂	100 M ⁻¹ s ⁻¹	Haag and Hoigne, 1983
3	HBrO ⁻ + O ₃ → BrO ₂ ⁻ + O ₂ + H ⁺	≤0.013 M ⁻¹ s ⁻¹	Haag and Hoigne, 1983
4	BrO ₂ ⁻ + O ₃ → BrO ₃ ⁻ + O ₂	>10 ⁵ M ⁻¹ s ⁻¹	Haag and Hoigne, 1983
5	HOBr ↔ H ⁺ + BrO ⁻	9.0 (8.8)	Haag and Hoigne, 1983
6	HOBr + NH ₃ → NH ₂ Br + H ₂ O	8.0 x 10 ⁷ M ⁻¹ s ⁻¹	Haag and Hoigne, 1984
7	NH ₂ Br + O ₃ → Y ^a	40 M ⁻¹ s ⁻¹	Haag and Hoigne, 1984
8	Y + 2O ₃ → 2H ⁺ + NO ₃ ⁻ + Br ⁻ + 3O ₂	K ₈ >> K ₇	Haag and Hoigne, 1984
9	NH ₄ ⁺ → H ⁺ + NH ₃	9.3	

Y^a are unknown products that react in later reaction

Table 2.3- Reaction and rate constants for hydroxyl radical mechanisms (von Gunten and Hoigne, 1994)

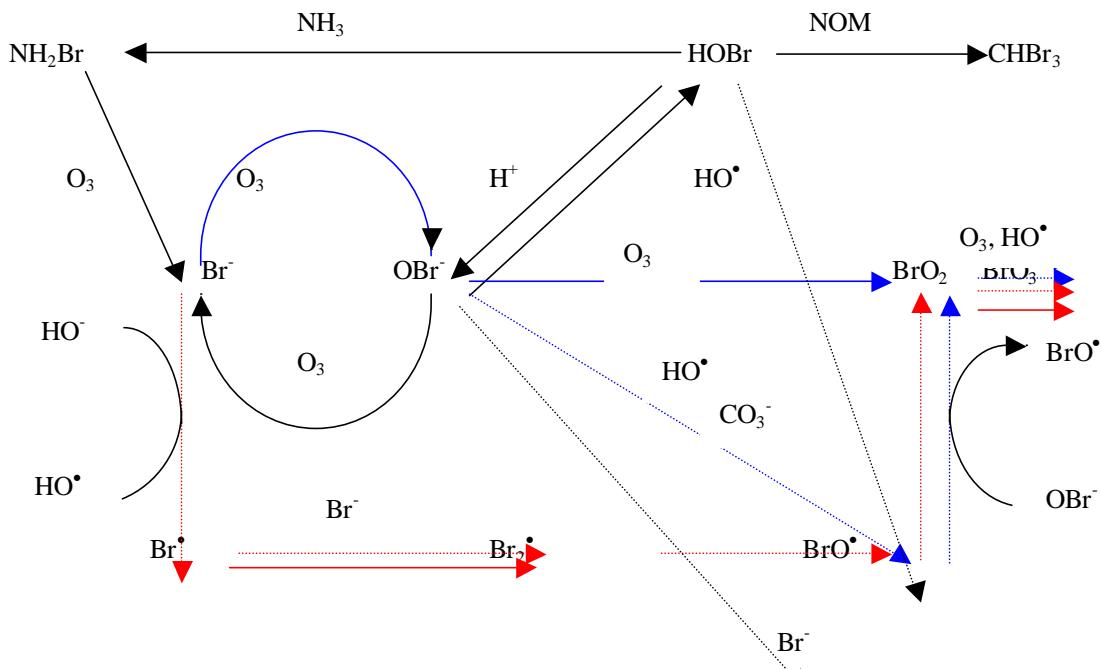
Equation Number	Reaction	<i>k</i> or pK _a	Reference
1	$\text{Br}^- + \text{HO} \rightarrow \text{BrOH}^-$	$3.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Zehavi and Rabini, 1972
2	$\text{BrOH}^- \rightarrow \text{Br}^- + \text{HO}^-$	$4.2 \times 10^6 \text{ s}^{-1}$	Zehavi and Rabini, 1972
3	$\text{BrOH}^- \rightarrow \text{Br} + \text{OH}^-$	$2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Zehavi and Rabini, 1972
4	$\text{Br} + \text{Br}^- \rightarrow \text{Br}_2^-$	$1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Taube, 1942
5	$\text{Br}_2^- + \text{Br}_2^- \rightarrow \text{Br}_3^- + \text{Br}^-$	$2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Sutton <i>et al.</i> , 1965
6	$\text{Br}_3^- \leftrightarrow \text{Br}_2^- + \text{Br}^-$	1.23	Sutton <i>et al.</i> , 1965
7	$\text{Br}_2^- + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{Br}^- + \text{H}^+$	$8.24 \text{ M}^{-1}\text{s}^{-1}$	Sutton <i>et al.</i> , 1965
8	$\text{BrO}^- + \text{Br}_2^- \rightarrow \text{BrO} + 2\text{Br}^-$	$8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
9	$\text{BrO}^- + \text{HO} \rightarrow \text{BrO} + \text{OH}^-$	$4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
10	$\text{HOBr} + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{H}_2\text{O}$	$7 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$	vonGunten <i>et al.</i> , 1996
11	$\text{BrO}^- + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{H}_2\text{O}_2$	$2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	vonGunten <i>et al.</i> , 1996
12	$\text{BrO}^- + \text{Br} \rightarrow \text{BrO} + \text{Br}^-$	$4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Klanning and Wolff, 1985
13	$\text{BrO} + \text{BrO} + \text{H}_2\text{O} \rightarrow \text{BrO}^- + \text{BrO}_2^- + 2\text{H}^+$	$4.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
14	$\text{BrO}_2^- + \text{HO} \rightarrow \text{BrO}_2^- + \text{OH}^-$	$2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
15	$\text{BrO}_2^- + \text{BrO}_2^- \rightarrow \text{Br}_2\text{O}_4$	$1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
16	$\text{Br}_2\text{O}_4 \rightarrow \text{BrO}_2^- + \text{BrO}_2^-$	$7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
17	$\text{Br}_2\text{O}_4 + \text{OH}^- \rightarrow \text{BrO}_3^- + \text{BrO}_2^- + \text{H}^+$	$7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
18	$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	10.25	
19	$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$	6.37	
20	$\text{CO}_3^{2-} + \text{HO} \rightarrow \text{CO}_3^- + \text{OH}^-$	$3.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton <i>et al.</i> , 1988

Table 2.4: Bromide oxidation reactions (Westerhoff et al., 1998)

Equation Number	Reaction	k or pK _a	Reference
1	$\text{Br}^- + \text{O}_3 \rightarrow \text{BrO}^- + \text{O}_2$	$50 \text{ M}^{-1}\text{s}^{-1}$	fitted parameter
2	$\text{BrO}^- + \text{O}_3 \rightarrow \text{Br}^- + 2\text{O}_2$	$300 \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigne, 1983
3	$\text{BrO}^- + \text{O}_3 \rightarrow \text{BrO}_2^- + \text{O}_2$	$100 \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigne, 1983
4	$\text{HOBr} \leftrightarrow \text{H}^+ + \text{BrO}^-$	9.0	von Gunten and Hoigne, 1994
5	$\text{BrO}_2^- + \text{O}_3 \rightarrow \text{BrO}_3^- + \text{O}_2$	$1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigne, 1983
6	$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	$1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Zehavi and Rabini, 1972
7	$\text{Br}^- + \text{HO} \rightarrow \text{BrOH}^-$	$3.3 \times 10^7 \text{ s}^{-1}$	Zehavi and Rabini, 1972
8	$\text{BrOH}^- \rightarrow \text{Br}^- + \text{HO}$	$4.2 \times 10^6 \text{ s}^{-1}$	Zehavi and Rabini, 1972
9	$\text{BrOH}^- \rightarrow \text{Br} + \text{OH}^-$	$2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Zehavi and Rabini, 1972
10	$\text{Br} + \text{Br}^- \rightarrow \text{Br}_2^-$	$1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Taube, 1942
11	$\text{Br}_2^- + \text{Br}_2^- \rightarrow \text{Br}_3^- + \text{Br}^-$	$2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Sutton <i>et al.</i> , 1965
12	$\text{Br}_3^- \leftrightarrow \text{Br}_2 + \text{Br}^-$	1.23	Sutton <i>et al.</i> , 1965
13	$\text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{Br}^- + \text{H}^+$	$8.24 \text{ M}^{-1}\text{s}^{-1}$	Sutton <i>et al.</i> , 1965
14	$\text{BrO}^- + \text{Br}_2^- \rightarrow \text{BrO} + 2\text{Br}^-$	$8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
15	$\text{BrO}^- + \text{HO} \rightarrow \text{BrO} + \text{OH}^-$	$4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
16	$\text{HOBr} + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{H}_2\text{O}$	$7 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$	vonGunten <i>et al.</i> , 1996
17	$\text{BrO}^- + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{H}_2\text{O}_2$	$2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	vonGunten <i>et al.</i> , 1996
18	$\text{BrO}^- + \text{Br} \rightarrow \text{BrO} + \text{Br}^-$	$4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Klanning and Wolff, 1985
19	$\text{BrO} + \text{BrO} + \text{H}_2\text{O} \rightarrow \text{BrO}^- + \text{BrO}_2^- + 2\text{H}^+$	$4.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
20	$\text{BrO}_2^- + \text{HO} \rightarrow \text{BrO}_2 + \text{OH}^-$	$2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
21	$\text{BrO}_2 + \text{BrO}_2 \rightarrow \text{Br}_2\text{O}_4$	$1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
22	$\text{Br}_2\text{O}_4 \rightarrow \text{BrO}_2 + \text{BrO}_2$	$7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
23	$\text{Br}_2\text{O}_4 + \text{OH}^- \rightarrow \text{BrO}_3^- + \text{BrO}_2^- + \text{H}^+$	$7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
24	$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	10.25	
25	$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$	6.37	
26	$\text{CO}_3^{2-} + \text{HO} \rightarrow \text{CO}_3^- + \text{OH}^-$	$3.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton <i>et al.</i> , 1988
27	$\text{HCO}_3^- + \text{HO} \rightarrow \text{HCO}_3 + \text{OH}^-$	$8 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Buxton <i>et al.</i> , 1988
28	$\text{ROC} + \text{HO} \rightarrow \text{Products} + \text{ROC}$	$2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Westerhoff <i>et al.</i> , 1997
29	$\text{HCO}_3 \leftrightarrow \text{CO}_3^- + \text{H}^+$	9.6	Chen <i>et al.</i> , 1973
30	$\text{CO}_3^- + \text{BrO}^- \rightarrow \text{BrO} + \text{CO}_3^{2-}$	$4.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Klanning and Wolff, 1985
31	$\text{HOBr} + \text{HO} \rightarrow \text{BrO} + \text{H}_2\text{O}$	$2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Dainton, 1968
32	$\text{HOBr} + \text{O}_2^- \rightarrow \text{Br} + \text{OH}^- + \text{O}_2$	$9.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Schwartz and Bielski, 1986
33	$\text{HO} + \text{NOM} \rightarrow \text{Products}$	TBD	Westerhoff <i>et al.</i> , 1997
34	$\text{OBr}^- + \text{NOM} \rightarrow \text{Products} + \text{Br}^-$	TBD	Anandh and Westerhoff, 1997
35	$\text{HOBr} + \text{NOM} \rightarrow \text{Products} + \text{Br}^-$	TBD	Anandh & Westerhoff, 1997
36	$\text{BrO} + \text{NOM} \rightarrow \text{Products} + \text{HOBr}$	$1 \text{ to } 10^8 \text{ M}^{-1}\text{s}^{-1}$	Westerhoff <i>et al.</i> , 1998a

HO: hydroxyl radicals (HO^\bullet)

TBD = To be determined in this study; ROC = Refractory Organic Carbon



Note: (1) blue and red solid lines represent ozone reaction and blue and red dashed lines represent HO[•] reaction;

- | | | |
|-----|--|--------------------------------------|
| (2) | | : Represents direct pathway |
| (3) | | : Represents direct/indirect pathway |
| (4) | | : Represents indirect/direct pathway |
| (5) | | : Represents indirect pathway |

Figure 2.1 - Schematic representation of bromate formation by molecular ozone and hydroxyl radicals (von Gunten and Hoigne, 1994)

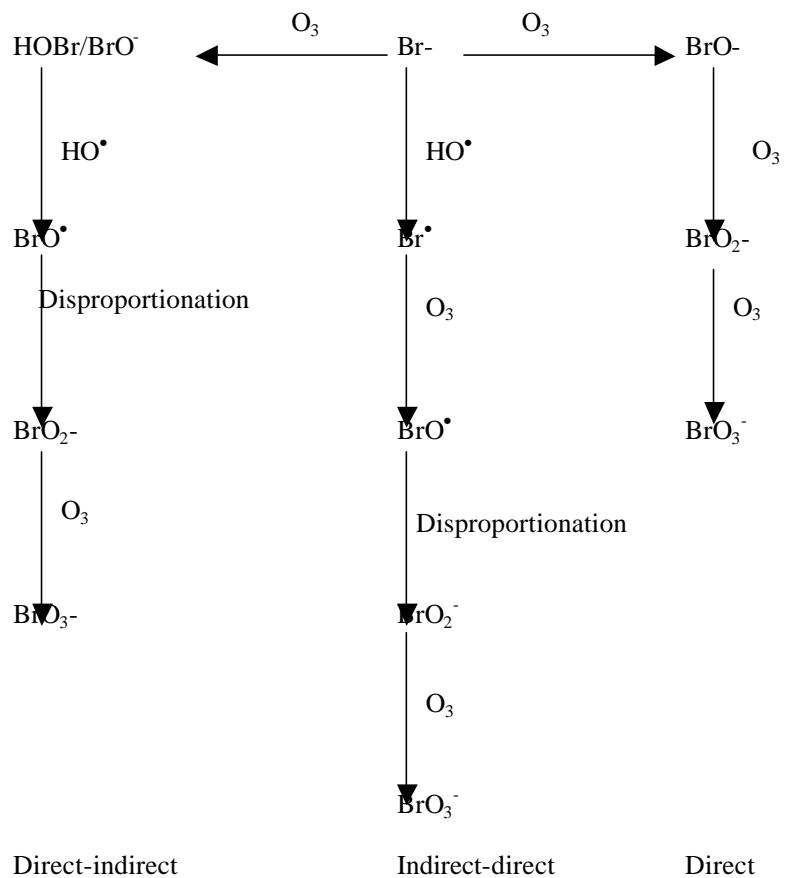


Figure 2.2: Three major bromate formation pathways (Song et al., 1996)

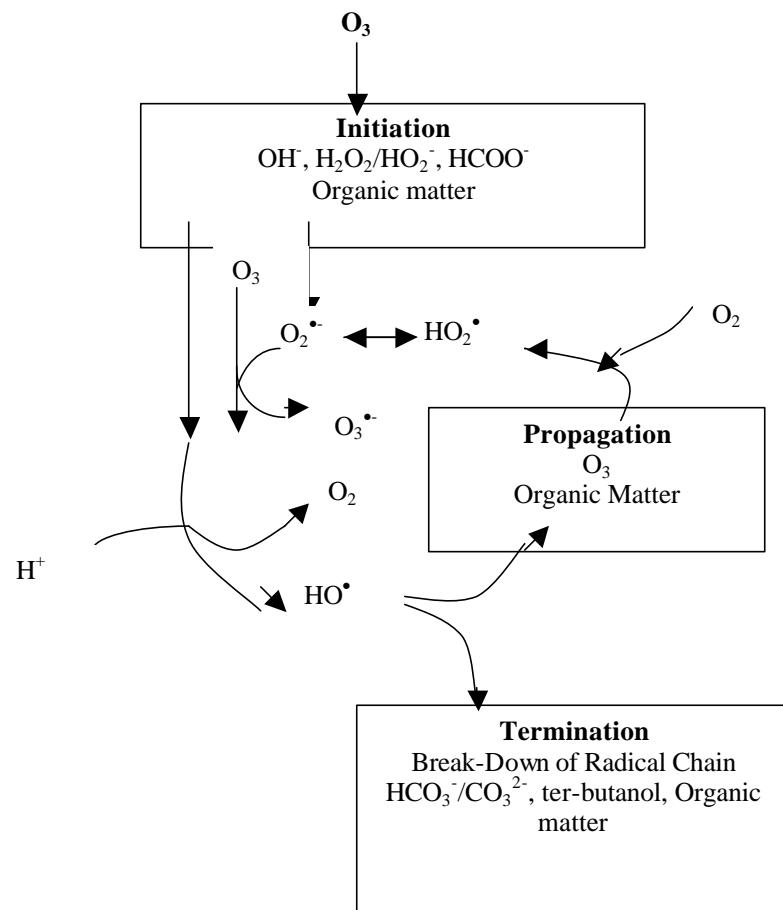


Figure 2.3- Reaction Schematic of the decomposition cycle of ozone in water (Staehelin and Hoigne, 1985).

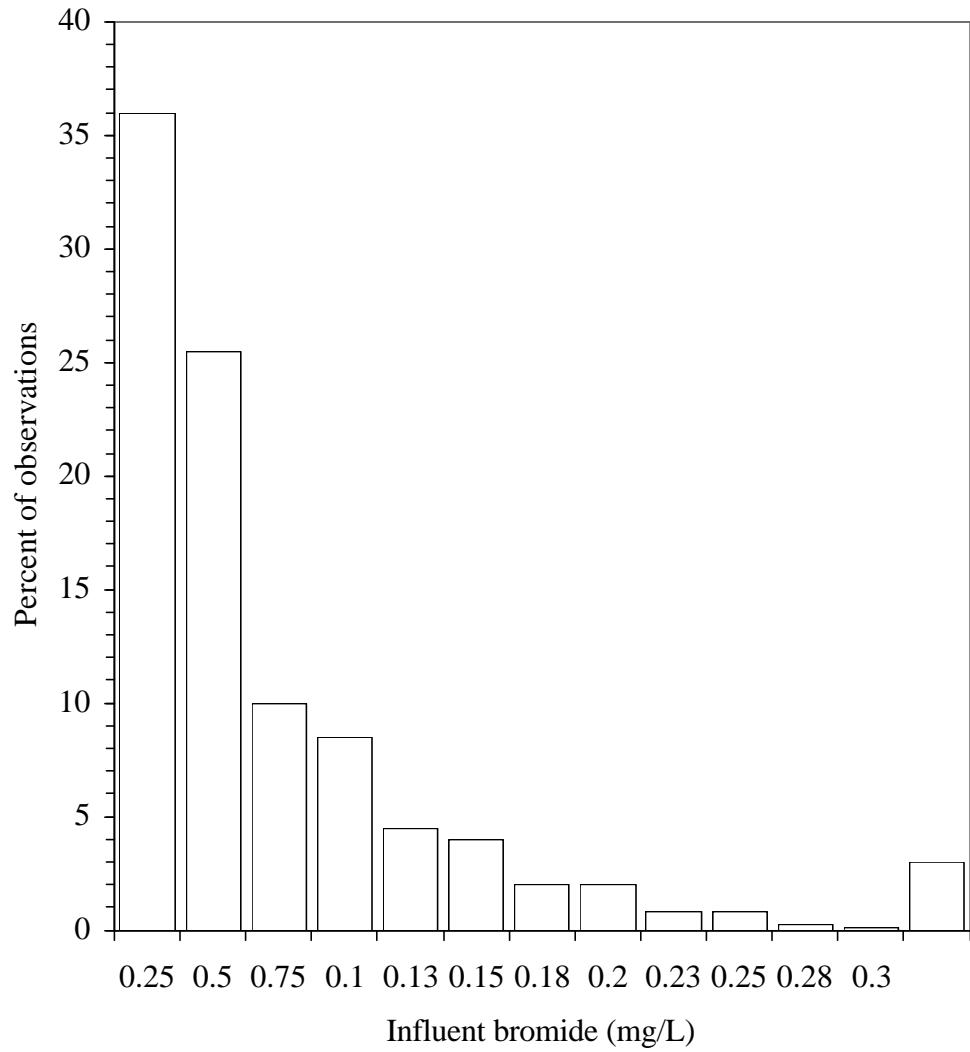


Figure 2.4- Bromide levels in treatment plants influents from 486 plants (7959 observations) of 18 months period (TWGDAW, 2002).

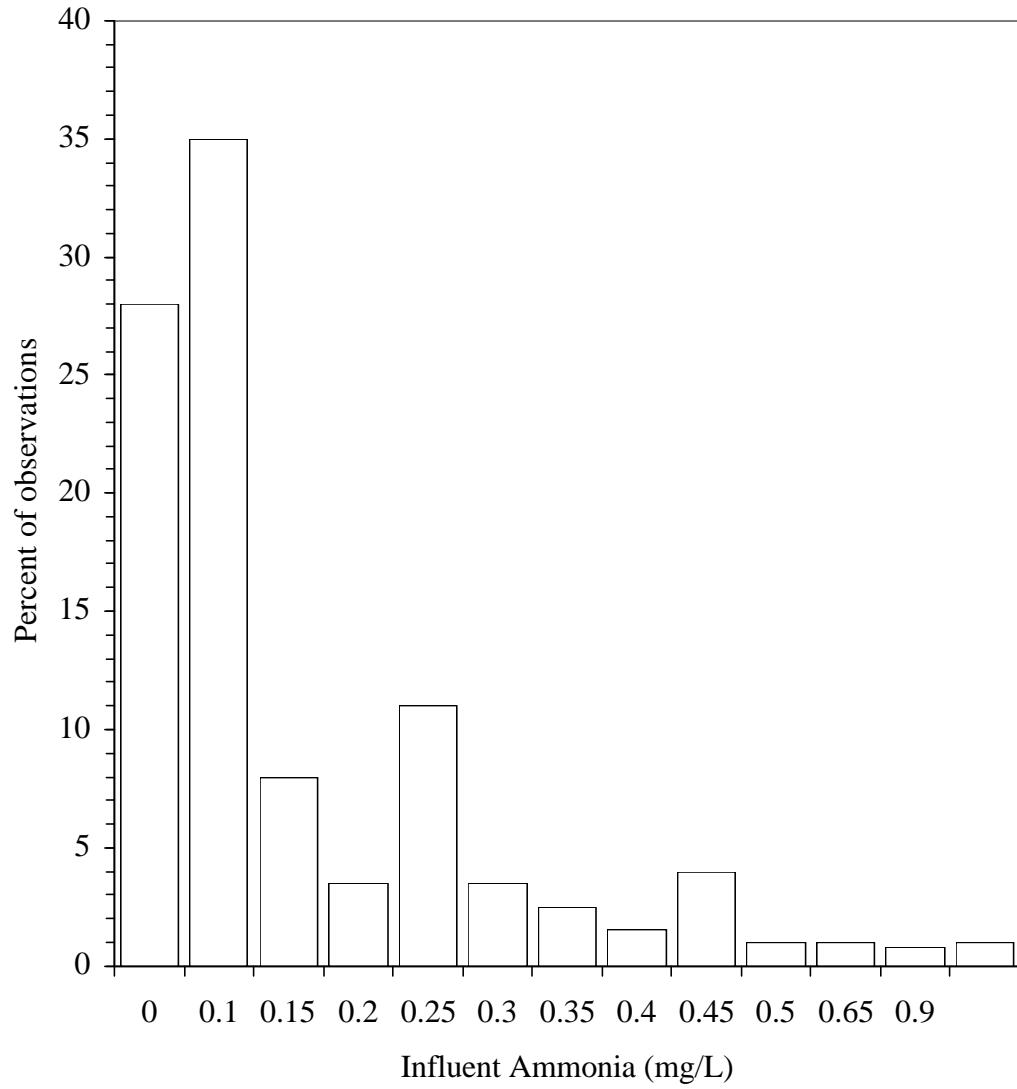
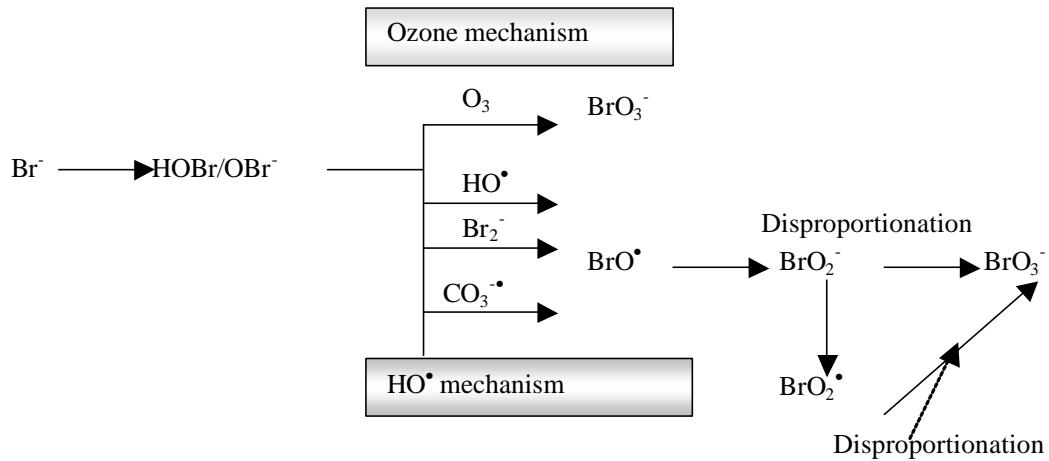


Figure 2.5- Ammonia levels in treatment plants influents from 486 plants (7959 observations) of 18 months period (TWGDAW, 2002).



Note: HO[•] mechanism includes reaction with secondary oxidant as CO₃[•] and Br₂⁻

Figure 2.6- Comparison of the molecular ozone mechanism and the HO[•] mechanism (von Gunten and Hoigne, 1994).

8. CHAPTER 3

9. OBJECTIVES AND RESEARCH HYPOTHESES

9.1. 3.1 OBJECTIVES

Bromate formation is the major concern in ozonated waters containing bromide. The mechanisms and kinetics of bromate formation have been well investigated and models that predicting bromate formation during ozonation have been developed in NOM free water. Most models have not considered NOM and ammonia effects, but would lead to more useful models for predicting the formation of bromate and a better understanding of possible bromate formation control strategies. The goals of this study are to provide better understanding of how bromate was formed by oxidation of molecular ozone and HO[•] under a wide range of different water qualities and treatment variables; and thus providing through information for predicting bromate formation with particular attention to NOM and ammonia effects in waters.

Meanwhile, in order to evaluate advantages and risks of ozonation processes, it is necessary to gain a full knowledge of the overall reaction mechanism and kinetics, considering all factors, before one can design adequate bromate control strategies that maximize disinfection efficiency. Therefore, kinetic data of oxidants, intermediate species as well as bromate formation are needed to provide the information of how water constituents and treatment variables affect on disinfection and DBP formation during ozonation.

Most studies had not thoroughly considered NOM and ammonia effects in natural waters. These two factors could be quite important on affecting bromate formation under various water qualities (e.g., different pH, (bi)carbonate alkalinity and NOM concentration and characteristics). Therefore, this study particularly focuses the following three key issues, which are lacking from previous studies:

- 1) Effects of HO[•] concentrations and ratio of oxidant pathways (O₃/ HO[•]) on bromate formation in natural waters..
- 2) Effects of aqueous bromine scavenging by ammonia on bromate formation.
- 3) Effects of aqueous bromine scavenging by NOM on bromate formation.

Bromine is the important intermediate affecting bromate formation during ozonation. However, since bromine was being studied for the formation of THMs and HAAs during chlorination of bromide-

containing waters, the rates of chlorination will be compared to those of bromination, thus leaving the significance of the findings. In this study two major sets of experiments, 1) bromate formation during ozonation and 2) bromine/chlorine reaction with NOM, will be conducted. Important research objectives are summarized below:

1. Identify the effects of water quality parameters (pH, DOC, Br⁻, temperature, ammonia and (bi)carbonate alkalinity) and operating conditions (O₃ dose, O₃ residual, constant time) on bromate formation;
2. Develop a comprehensive database of BrO₃⁻, O₃ and HO radical concentrations;
3. Quantify the contribution of bromate formation by molecular ozone and hydroxyl radicals, respectively.
4. Determine and compare rates of reaction between chlorine and bromine with NOM.
5. Evaluate the mechanism of ammonia addition on bromate control in natural waters.
6. Simulate bromate control measures necessary to meet proposed and future MCLs under a wide range of conditions (e.g., pH depression and ammonia addition).

9.2. 3.2 RESEARCH HYPOTHESES

In this study, the effects of strong oxidants (e.g. O₃ and HO radicals) on bromate formation during ozonation containing bromide raw water are reported. In addition, mechanisms of chlorination/bromination of NOM will be separately studied since bromination plays an important role in both ozonation and chlorination of water containing bromide. Four hypotheses are stated below to address the mechanisms and effects of different water quality characteristics and treatment variables on bromate formation in ozonation and mechanisms and rate of chlorination/bromination of NOM. A rational discussion of relevant background accompanies each hypothesis.

9.2.1. 3.2.1 Hypothesis I: Bromate formation increases proportionally to the ratio of $[HO^\bullet]/[O_3]$ during ozonation, affected by different water qualities (pH, DOC, temperature, ammonia and (bi)carbonate alkalinity) and water treatment conditions (ozone dose, contact time and flow rate).

Both ozone and its decomposition by-product, HO^\bullet , are very strong oxidants and can contribute to the formation of bromate during the ozonation process. Their decompositions are affected by water quality parameters (e.g., pH, temperature, NOM characteristics, microorganisms, inorganic compounds of oxidizable cations and anions, etc.), which therefore affect the rate of bromate formation. Most ozonation and bromate formation studies focused on initial water quality (pH, DOC, Br^- , temperature, (bi)carbonate alkalinity) and treatment conditions (O_3 dose, O_3 residual, contact time) which are the major parameters that affect O_3 decomposition in natural waters. A conceptual reaction mechanism of bromate formation in ozonation shows that bromate is formed via a molecular ozone pathway (R_1) and HO^\bullet pathway (R_2) (Figure 3.1). Both R_1 and R_2 form intermediates (e.g., bromine Br^\bullet or BrO^\bullet) prior to forming the final product, bromate. In addition, side reactions with ammonia and NOM in water could compete with ozone and/or HO^\bullet affecting the extent of bromate formation.

Since the overall mechanisms of bromate formation via both ozone and HO^\bullet pathways are very complex. The parameter, R_{CT} , expressing the ratio of the $[HO^\bullet]/[O_3]$, was introduced to represent the HO^\bullet concentrations (or exposure) and ozone concentration (or exposure) during ozonation (Elovitz and von Gunten, 1999). Elovitz and von Gunten (2000) reported that the R_{CT} remains constant during the overall ozonation process for a given water quality and set of reaction conditions (e.g. ozone dose, contact time). However, R_{CT} varies under different water quality parameters (e.g. pH, temperature, (bi)carbonate alkalinity and NOM) and ozonation treatment conditions. This is consistent with the fact that bromate formation during ozonation is affected by water quality parameters and treatment conditions. Therefore, it can be hypothesized that the formation of bromate is proportionally to the value of R_{CT} during ozonation. Given the experimentally measured rate constant for ozone depletion and the R_{CT} value, it would be possible to model the ozone and HO^\bullet reaction and thus predict bromate formation.

9.2.2. 3.2.2 Hypothesis II: HO[•] concentrations decrease proportionally with increasing DOC and (bi)carbonate alkalinity and decreasing pH in natural waters

During the ozonation process, HO[•] exists at very low concentrations due to its high and nonselective reactivity. Yates and Stenstrom (1993) reported that an increase in pH generates more HO[•] over a fixed time interval. In pure water, HO[•] concentration, controlled by ozone and pH, ranges from approximately 10^{-13} M at pH 6.5 to 10^{-11} M at pH 8.5 (Song et al., 1996). Moreover, the presence of NOM and bicarbonate/carbonate will result in scavenging of HO[•] (Hoigne et al., 1985). Westerhoff (1995) found HO[•] concentration ranged from 3.1×10^{-12} M to 1.2×10^{-11} M in the presence of three different NOM isolates at pH 7.5. In addition, waters containing total inorganic carbon (TIC), expressed as (bi)carbonate alkalinity, can influence both ozone decomposition and HO[•] concentration via the reactions with bicarbonate and carbonate (Elovits and von Gunten, 2000):



During the ozonation of natural waters, ozone decomposition is dependent upon water quality and treatment conditions, whereas HO[•] concentration is dependent on the molecular ozone concentration over time. It has been observed that ozone decomposition is faster at higher pH due to higher hydroxide ion concentration, whereas HO[•] concentration decreases as pH decreases. In addition, when NOM is present in natural waters, HO[•] concentration is controlled by concentrations of both ozone and NOM (Song et al., 1996); and as well as (bi)carbonate alkalinity (von Gunten, 2000). NOM in natural waters, acting as an ozone decomposition promoter and free radical generator, plays an important role in HO[•] formation and the scavenging of HO[•] (von Gunten, 2000). Overall the HO[•] concentration will decrease as DOC concentration increases due to the rapid scavenging reaction of HO[•] by DOC ($\sim 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). Since bicarbonate/carbonate are also HO[•] scavengers (Buxton et al., 1988), they can stabilize the decomposition of aqueous ozone by scavenging HO[•] and therefore decreasing HO[•] concentration during the ozonation process.

9.2.3. 3.2.3 Hypothesis III: Ammonia addition for controlling bromate formation does not alter the $[HO^\cdot]/[O_3]$ ratio, but shifts bromate formation towards the HO^\cdot oxidation pathway by scavenging HOBr/OBr⁻.

Ammonia addition can be used to reduce bromate formation during ozonation with waters contain bromide. The theory behind this bromate reduction strategy is that ammonia can quickly react with hypobromous acid, an intermediate of bromide oxidation to bromate, to form monobroamine. The reaction is as follow (Wajon and Morris, 1979):



This will therefore reduce HOBr/OBr⁻ availability for reaction with ozone to form bromate. However, bromate formation via bromide oxidation to intermediate bromine and then bromate by ozone is not the only pathway in ozonation bromate formation process. Significant amount of bromate will still form due to the other HO^\cdot pathways contributing considerable amount of bromate formation. With the addition of ammonia, HO^\cdot will react with ammonia; however, the reaction is not as fast as with other micropollutants (~ 1-2 orders of magnitude less). In addition, Br[•] and BrO[•] oxidized from the bromide ion by HO^\cdot most likely do not react with ammonia. Therefore, during ozonation in the presence of ammonia, the formation of bromate will shift towards HO^\cdot oxidation by scavenging HOBr/OBr⁻, but the ratio of $[HO^\cdot]/[O_3]$ will not be altered.

9.2.4. 3.2.4 Hypothesis IV: Aqueous bromine has a higher rate constant with NOM than aqueous chlorine. The rate of reaction between bromine and chlorine with NOM is affected by the characteristics of NOM and pH.

NOM is a heterogeneous mixture of poly-functional organic compounds which differ based on source materials, season, geochemical process and limnological process (Thuman, 1984). The basic principals that govern the reactivity of halogens with model organic compounds probably hold true for complex NOM molecules as well. Halogen reactions toward model organic molecules are very selective and, in general, reactions of kinetic significance are limited to unsaturated aromatic and phenolic compounds or specific functional groups.

Chlorine oxidation studies with several purified hydrophobic organic acids isolated from of NOM representing several different sources results in significant correlation between aromatic, phenolic and activated aromatic properties of the NOM fraction as well as chlorine demand (Reckhow et al., 1992). By following the same basic principals for the reactivity of chlorine and bromine toward model compound, it is anticipated that NOM reactivity with chlorine and bromine will be related to its characteristic. The reaction of halogens and NOM are mainly by substitution and oxidation. However, the reaction rate and ratio of substitution and oxidation by chlorine and bromine may differ due to the extent of oxidation and NOM characteristics. Since the dissociation of chlorine and bromine and NOM protonation and deprotonation are strongly dependent upon pH, the kinetic and mechanism reaction of chlorination and bromination are dependent on pH as well.

Table 3.1 - Rate constants of oxidation by O₃ or HO[•] radicals.

Compound M	K _{O₃}	Reference	K _{HO}	Reference
Br ⁻	160	Hoigne and Bader, 1983 III	1.00E+09	
HOBr	< 0.01	Hoigne and Bader, 1983 III	2.00E+09	Buxton, 1968
BrO ⁻	530	Hoigne and Bader, 1983 III	4.20E+09	Buxton, 1968
BrO ₂ ⁻	> 10 ⁵	Hoigne and Bader, 1983 III	5.81E+11	Buxton, 1968
BrO ₂ radical			2.00E+09	Buxton, 1969
BrO ₃ ⁻	< 10 ⁻³	Hoigne and Bader, 1983 III	3.00E+06	Amichai, 1969
Cl ⁻	~0.003	Hoigne and Bader, 1983 III	4.30E+09	Buxton, 1968
H ₂ O ₂			3.50E+07	Hoigne and Bader, 1978
HCO ₃ ⁻	<0.01		8.00E+06	Buxton, 1968
CO ₃ ²⁻	<0.01		2.40E+08	Buxton, 1968
PCBA	0.15		5.00E+09	
ABTS			1.20E+10	
t-BuOH	~0.003	Hoigne and Bader, 1983 I	5.90E+08	
Atrazine	7		5.00E+09	Von Gunten, 2000
Benzene	2		8.00E+09	
p-xylene	140		7.00E+09	Elovitz, 2000
phenol	1.3*10 ³ ; 1.4*10 ⁹	Hoigne and Bader, 1983 II	6.60E+09	Buxton et al., 1988
Resorcinol	> 300*10 ³	Hoigne and Bader, 1983 II	1.20E+10	Buxton et al., 1989
Glycine			1.70E+07	Buxton et al., 1990
Glucose			1.50E+09	Buxton et al., 1991
NH ₃	20.4	Hoigne and Bader, 1983 II	1.70E+07	Meyerstein, 1972
NH ₂ Br	160	Hoigne and Bader, 1983 III		
NHBr ₂	40	Hoigne and Bader, 1983 III		
S ₂ ⁻				Hoigne and Bader, 1985
HS-	3.00E+09	Hoigne and Bader, 1983 III		Hoigne and Bader, 1985
H ₂ S	3.00E+04	Hoigne and Bader, 1983 III		Hoigne and Bader, 1985
SO ₃ ²⁻	1.00E+09			Hoigne and Bader, 1978
HSO ₃ ⁻	3.20E+05			Erickson, 1977
H ₂ SO ₃	2.00E+04			Penkett, 1972
NOM			2.80E+09	
OH ⁻	210	Hoigne and Bader, 1983 III		
H ₂ PO ₄ ⁻	<2*10 ⁻⁴	Hoigne and Bader, 1983 III		
Raw H ₂ O NOM			3.80E+04	Haag, 1993
Formic acid	5; 100*	Hoigne and Bader, 1983 II		
Dimethylamine	19*10 ⁶	Hoigne and Bader, 1983 II		

*: (K_{H_B}; K_{B⁻})

All units are M⁻¹S⁻¹.

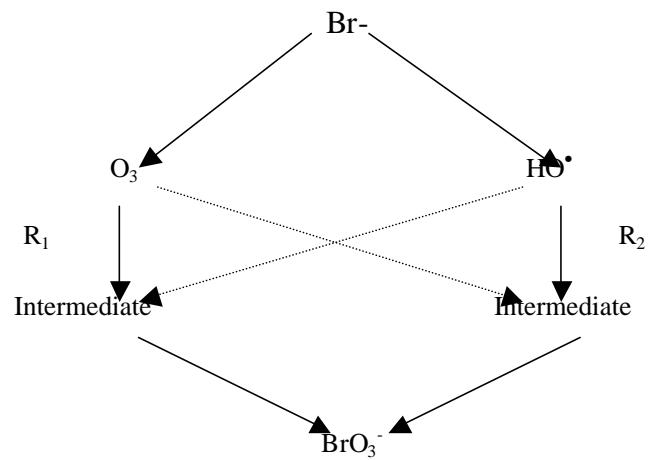


Figure 3.1 - Conceptual reaction mechanism of bromate formation in ozonation.

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10. CHAPTER 4

11. KINETICS OF HYDROXYL RADICAL FORMATION

12. DURING OZONATION PROCESSES

12.1. 4.1 INTRODUCTION

Ozone is a powerful oxidant and disinfectant. The application of ozonation used in drinking water treatment has been growing exponentially in the US since the early 1980's (Rice, 1997) due to a number of benefits including 1) disinfection and algae control, 2) oxidation of adverse organic and inorganic (micro)-pollutants, and 3) improvement of coagulation (Langlais, et al, 1991, Han et al., 1998 and Staehelin and Hoigne, 1982). However, chlorination by-products and the inability of chlorine to effectively control chlorine-resisted pathogens such as *Cryptosporidium parvum* (*C. Parvum*) protozoan are probably the major concern for which ozone has became an attractive alternative disinfectant.

During ozonation, molecular ozone (O_3) decomposes and forms hydroxyl radicals (HO^\bullet). Ozonation is initiated by decomposition of O_3 with hydroxide ions (OH^-) and propagated by the reaction of superoxide radical ions (O_2^-) with O_3 to produce HO^\bullet (Buhler et al, 1984). Other various reactions involving these species and short-lived free radical species occurring during ozonation of water and the complicated reaction cascade is proposed as a SBH model (Staehelin et al., 1984). Despite ozone's substantial reactivity with microbial constituents (thus providing disinfection), ozone is relatively non-reactive towards many inorganic species and classes of organic compounds (Hoigne and Bader, 1983, 1985), and thus the oxidation of these reactants by ozone may be kinetically hindered. In contrast, HO^\bullet is a highly reactive and nonspecific oxidant (Hoigne, 1988) and is the main oxidant for certain ozone-resistant micropollutants.

While ozone can successfully address drinking water problems by removing or reducing unwanted constituents, bromate, one of the major concerned ozonated disinfection by-products (DBPs), can be easily formed if waters contain bromide ion (Haag and Hoigne, 1983). The formation of bromate during ozonation process does not reduce naturally and is strictly regulated due to its suspected carcinogenic toxicity. Recently, with the emergence of microorganisms, such as *C. Parvum* that are more resistant to

chemical disinfection, regulations may soon require higher disinfection capability to guarantee such highly-resistant microbial inactivation. An unwanted consequence of increased ozone exposure is the potential for increased bromate formation from a sequence of oxidation reactions (involving both O₃ and HO[•]) in bromide containing waters (von Gunten and Hoigne, 1994). The United States Environmental Protection Agency (EPA) has posted the Stage II maximum contaminant level (MCL) of bromate to the level of 10 µg/L (EPA, 2000).

Taken together of considering demands of disinfection (high O₃ exposure) and oxidation (high combined oxidant exposure) and DBP control (low combined oxidant exposure), optimization of operating ozonation process for drinking water treatment becomes very challenging. Knowledge of the steady state O₃ and HO[•] concentrations within an ozone reactor is, therefore, critical for making adequate predictions for disinfection, oxidation, and DBP formation during the water treatment processes. Major challenge of this task lies in the complexity of the ozone chemistry and the difficulty in directly measuring the concentration of HO[•].

The ability to predict and model ozonation processes for drinking water treatment is contingent on knowing the concentrations of both O₃ and HO[•] during the process. While O₃ concentrations are readily obtainable with standard methods (Hoigne and Bader, 1981), HO[•] concentrations are not directly accessible because of their low concentrations and highly reactive during ozonation process. In previous publications, R_{CT} is introduced (Elovitz and von Gunten, 1999 & 2000), and is defined as the ratio of the exposures of HO[•] and O₃, i.e., the concentration of oxidant integrated over the reaction time, shown below:

$$R_{CT} = \frac{HO^{\bullet} - \text{exp osure}}{O_3 - \text{exp osure}} = \frac{\int [HO^{\bullet}]dt}{\int [O_3]dt} \quad 4-1$$

The value of $\int [HO^{\bullet}]dt$ in Equation 4-1 can be indirectly determined by monitoring the decrease of an ozone-resistant probe compound, whereas the $\int [O_3]dt$ is calculated from direct ozone measurement as the area under the O₃ concentration versus time curve (von Gunten and Hoigne, 1994).

To determine concentrations of HO[•], an indirect method, based upon measurement of decrease of an O₃-resistant probe compound that reacts quickly with HO[•], can be applied (Elovitz and von Gunten, 1999; Hagg and Yao, 1993). This measurement allows transient, steady state HO[•] concentrations in

aqueous solutions to be calibrated. The probe compound selected was p-chlorobenzoic acid (PCBA), with very fast rate constant of $k_{HO\cdot, PCBA} = 5.2 \times 10^9 M^{-1}s^{-1}$ for its reaction with HO \cdot and a very slow rate constant of $k_{O_3, PCBA} = 0.15 M^{-1}s^{-1}$ for its reaction with O₃ (Haag, and Hoigne, 1981) Yao and Haag, 1991). PCBA has a pK_a of 4 (Yao and Haag, 1991); therefore, the rate constant is given for the deprotonation form. PCBA is used in very low concentrations to prevent a significant contribution to overall scavenging of HO \cdot . The term “HO \cdot oxidation capacity” is defined by the relative elimination of the HO \cdot probe compound. The rate of PCBA oxidation, which reacts only with HO \cdot , is given by:

$$\frac{-d[PCBA]}{dt} = k_{HO, PCBA}[PCBA][HO\cdot] \quad 4-2$$

Rearranging and integrating Equation 4-2 results in:

$$\ln\left(\frac{[PCBA]_t}{[PCBA]_o}\right) = -k_{HO, PCBA} \int_o^t [HO\cdot] dt \quad 4-3$$

Substituting HO \cdot exposure from Equation 4-1 in Equation 4-3 gives:

$$\ln\left(\frac{[PCBA]_t}{[PCBA]_o}\right) = -k_{HO, PCBA} R_{CT} \int_o^t [O_3] dt \quad 4-4$$

This allows the calculation of the R_{CT} from the experimental measured decrease in concentration of PCBA and O₃ (by plotting the ln[PCBA]_t/[PCBA]_o versus O₃ exposure). Elovitz and von Gunten (1999 & 2000) found that the R_{CT} remains almost unchanged during batch ozonation for a given water and set of reaction conditions. Therefore, the concentrations of HO \cdot can be easily calculated from the measured O₃ and PCBA. However, waters from different sources contain different water chemistry and thus affect exposure of ozone as well as HO \cdot throughout ozonation. Water quality parameters such as pH, temperature, bromide, (bi)carbonate alkalinity, NOM and ammonia affect rates of ozone decomposition and HO \cdot generation and concentration (Song, et al., 1996). In addition, varying ozone treatment such as change of ozone dose and contact time can also perform different ozone decomposition rates. Therefore, it can be referred that the values of R_{CT} are strongly controlled by these natural water parameters and treatment differences.

The objectives of this study are to investigate the effects of water characteristics (pH, temperature, Br $^-$, (bi)carbonate alkalinity, NOM and ammonia) and treatment variables (ozone dose, reaction time) on

R_{CT} as well as O_3 and HO^{\bullet} concentrations during ozonation. Bench-scale batch and continuous flow and pilot-scale ozonation experiments were conducted. Colorado River water (CRW) was used as the source water since it is a major water supply for six southwestern states in the United States. It is hypothesized (*Hypothesis II*) that “ HO^{\bullet} concentrations decrease proportionally with increasing DOC and (bi)carbonate alkalinity and decreasing pH in natural waters” and was addressed in this chapter.

12.2. 4.2 METHODOLOGY

Bench-scale batch and continuous flow ozonation experiments were conducted in laboratory and pilot-scale ozonation tests were performed at Union Hills Water Treatment Plant in Phoenix, AZ. Details of materials and methods used for this study are described below:

Materials: All chemicals added were analytical grade and stock solutions for adjusting initial water qualities were prepared in Nanopure water (>18mΩ) made from ultrapure water system (Nanopure Infinity™). Gaseous ozone was generated by OREC™ (Model V5-0, Phoenix, AZ) ozone generator from pure oxygen. Figure 4.1 shows the schematic diagram of stock ozone solution generation system and batch ozonation reactor. The concentrated dissolved O_3 stock solutions were produced by continuously bubbling pure gaseous O_3 through a two-liter glass reactor filled with Nanopure water that was cooled in an ice bath. Gaseous ozone was transported by stainless steel tubing and passed a gas-washing bottle containing 0.5 M phosphate buffer (pH 6) to remove nitric oxidized impurities before dissolving into water. The saturated stock O_3 solution of approximately 40 mg/L ($\epsilon_{258nm}=3100\text{ M}^{-1}\text{cm}^{-1}$; pH 2) was achieved routinely after an hour.

All experiments were performed with one single source water from the Colorado River conveyed by the Central Arizona Project canal (CRW water). The raw water used for batch experiments was collected at the Scottsdale Water Campus in Scottsdale, Arizona and passed through ashed glass filter papers (GF/F Whatman™) to remove particles. Filtered water was stored at 4 °C before use. The pH of all waters was adjusted to the desired values by adding prepared stock solutions of sulfuric acid or sodium hydroxide. Experiments of temperature effect were conducted in an incubator with controlled temperature. For the experiments of DOC effect, the desired DOC concentrations were adjusted by adding additional DOC from a stock solution that prepared by re-dissolving the CRW DOC isolate that previously extracted

using Nano-filtration and XAD-4 membrane technique. Details of DOC isolation processes are shown in Appendix A. For the experiments of (bi)carbonate alkalinity effect, sample waters were first decarbonated of all carbonate/bicarbonate contents by lowering the pH to 4.3 and stripping off carbon dioxide contents by using pure helium. The decarbonated waters were added bicarbonate stock solution to the desired (bi)carbonate alkalinity after pH was readjusted. Ammonia chloride was used for adjusting ammonia levels in the water. All water samples were spiked with 0.25 μM of para-chlorobenzoic acid (PCBA) before ozonation to measure HO $^{\bullet}$ concentration.

Batch Ozonation Experiments. Batch ozonation experiments were performed by injecting small volumes of the ozone stock to achieve an initial ozone concentration (2-4.5 mg/L) into a 1-L cylinder reactor (Figure 4.1) containing 500 milliliters of prepared waters with adjusted water quality. A Teflon mesh was applied to cover the top of water surface as soon as stock ozone solution was added to prevent the ozone loss by volatilization. Samples were collected over time for monitoring residual ozone by the indigo method (Bader and Hoigne, 1981) and for PCBA, HOBr, bromate and nitrate analysis, samples were collected and immediately bubbled with high flow of pure helium to remove ozone residual.

Continuous-flow Ozonation Experiments. The gaseous ozone with adjusted flow rate passed through the first 500-mL gas-washing bottle with 0.5-M phosphate solution (pH 6) and then the pure gaseous ozone was introduced to the bottom of the first 1-L reactor with a diffuser, whereas countercurrent filtered (Whatman™ 1.2 μm 100-25 DH and 0.7 μm 100-25 AH) CRW water with various flow rates flowed into the reactor from the top port (Figure 4.2). Ozone residual collected at different sampling ports, which representing different hydraulic retention times, were monitored. When ozone concentrations remained constant over time (reached a steady state condition), water samples were collected at sampling ports 1, 2 and 3. Ozone residuals were measured immediately after samples were collected and, in the mean time, some sampled waters were stripped with helium for later bromate, nitrate and PCBA analysis. For the separate ammonia addition and pH depression experiments, stock solution of ammonia chloride and concentrated sulfuric acid were added to the water prior to the experiments. After all the experiments were completed, a blue dye (λ_{max} : 600 nm) was added into water as a tracer to determine the flow and reactor hydraulics. Results of analysis of hydraulic retention time and number of CSTRs in series are shown in Appendix B.

Pilot-Scale Ozonation Experiments. The pilot unit of ozonation shown in Figure 4.3 consisted of four columns which locates at Union Hills Water Treatment Plant that operated by Carollo Engineers™ in Phoenix, AZ. Gaseous ozone, produced from oxygen with an OREC™ ozone generator, was bubbled into the base of the first column with countercurrent 4.5 gallons per minutes (gpm) of raw CRW water from sedimentation tank flowed into the top of the first column. Chemical feed such as PCBA and/or ammonia chloride, ferric chloride and polymer were introduced prior to the ozone columns. Water samples were collected at several different ports along the columns representing different hydraulic retention times for ozone residuals as well as bromate formation and PCBA consumption. For bromate and PCBA samples, the collected samples waters were first stripped by helium to remove residual ozone and then stored in 4 °C prior to analysis.

Analytical Method. The dissolved O₃ concentrations in the stock solution were determined by direct UV absorbance at 258 nm (ϵ : 3100 M⁻¹cm⁻¹ at pH 2) (Langlais et al., 1991). Stock ozone solution was diluted to an UV absorbance of less than 1.0 cm⁻¹ with diluted phosphoric acid to remain in the linear portion based upon Beer-Lambert's Law. For waters containing NOM, dissolved ozone residuals were measured with Shimadzu™ UV/VIS spectrophotometer using a self-prepared indigo solution based upon the indigo calorimetric method (Bader & Hoigne, 1981) for all batch experiments. For continuous flow and pilot-scale ozonation experiments, ozone residuals were measured using Hach™ Accuvac Ampuls via the indigo method. Solution pH and temperature were measured using a Bechman™ pH electrode, which was calibrated with standard buffers (J. T. Baker™). Aqueous bromine (HOBr/OBr⁻) was measured using Hach™ pocket calorimetric spectrophotometer. DOC concentrations were determined by a Shimadzu™ TOC 5050 Analyzer. Water's alkalinites were measured by Hach™ kit colorimetric titrator. Bromide, bromate and nitrate were measured by using a Dionex™ ion chromatography with eluent made up of 9mM carbonate. PCBA was measured using HPLC with reverse-phase (RP-18) analytical column and mobile phase consisting of a mixture of 55% methanol and 45% 10 mM phosphoric acid. Detection was made using an UV detector set to a wavelength of 234 nm.

12.3. 4.3 RESULTS

12.3.1. 4.3.1 Aqueous Ozone Measurement:

Direct UV absorbance measurement at wavelength 258 nm provides a reliable method for aqueous O_3 measurement. The indirect Indigo method at absorbance of wavelength 600 nm was applied for measuring O_3 residual in CRW water due to NOM interference. The self-prepared Indigo reagent, based on Hoigne's (1981) approach, was well calibrated by UVA direct method up to 3.5 mg/L of O_3 without any dilution. In contrast to the HachTM Ampulus indigo-based method that can only measure O_3 residual up to 1.5 mg/L without any dilution, the self-prepared Indigo reagent can provide higher O_3 residual (> 1.5 mg/L) measurement more accurately without any unnecessary steps of sample water dilution that result in underestimation due to ozone's demand and decay over the processes. The molar extinction absorptivity for UV direct method and Indigo method were 3100 and 20200 $M^{-1} cm^{-1}$, respectively. Figure 4.4 shows a good relationship between these two methods on measuring O_3 concentrations for pure water. In addition, the results showed that using the self-prepared Indigo reagent correlated well with the HachTM Ampulus indigo for measuring O_3 residuals of less than 1.5 mg/L in both Nanopure water and ambient CRW water (opened circles).

12.3.2. 4.3.2 Bench-Scale Batch Ozonation

Results of CRW water batch ozonation experiments show three stages of ozone consumption, which were defined as instantaneous stage, fast stage, and slow stage. Ozone demand and decay characteristics varied and were affected by different water quality parameters, e.g., bromide level, pH, temperature, (bi)carbonate alkalinity and DOC concentration and their extents as well as treatment variables, e.g., O_3 dosage, contact time and addition of acid or ammonia in batch ozonation experiments. Figure 4.5 shows an example of ozone concentration change and exposure over time at different pH conditions that as soon as ozone was added to the water, an instantaneous ozone consumption step occurred immediately followed by a gradually decrease of ozone decay. However, rates for this instantaneous ozone reaction could not be identified due to the experimental setup. Similar trends were observed to change of PCBA concentrations over time (Figure 4.6). It was observed that the higher the water pH, the faster

consumption of the PCBA. This is due to a higher initiation rate of O_3 decomposition in the presence of higher hydroxide concentrations that consume more PCBA at higher water pH (see Eqn 4-5).

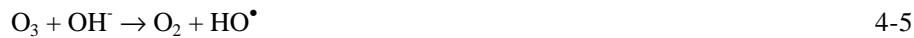


Figure 4.7 shows the first-order reaction plots with respect to O_3 concentrations over time. The first-order rate constant of O_3 decay was obtained by plotting natural logarithm of O_3 concentrations (e.g., $\ln [O_3]_t/[O_3]_{t=0}$) versus times, whereas the slope from the linear regression line represents rate constant. A two-stage (fast stage and slow stage) ozone first-order reaction where the turning point occurred at 2 minutes was observed, which shows a better fit than one-stage instead. The same trends of overall three-stage reactions were observed when plotting first-order kinetics of PCBA depletion based upon the data of PCBA concentrations over time. These shows, like O_3 concentration, that maximum HO^\bullet concentrations were achieved initially followed by a two-stage kinetic HO^\bullet concentration curves in which higher concentrations and higher rates of depletion at the fast stage than the slow stage. In addition, ozone demand, determined by operating an ozone system at several ozone dosages, represents the maximum applied ozone dose that does not result in ozone residual due to instantaneous consumption. Figure 4.8 shows ozone demand curves that based upon five ozone dosages for CRW raw water. The intersection of the demand curve with the X-axis is the ozone demand of the CRW raw water, which is 0.87 mg/L.

By plotting $\ln([PCBA]_t/[PCBA]_{t=0})$ versus O_3 exposures (Figure 4.9), the slopes of linear interpretation show the values of $R_{CT} \times k_{HO^\bullet, PCBA}$ for the fast and slow stages. Therefore, R_{CT} provides a very useful tool for calculating HO^\bullet concentrations from known O_3 measurements. More details of R_{CT} and HO^\bullet influenced by water characteristics and treatment variables will be discussed later in this paper.

12.3.3. 4.3.3 Comparison of R_{CT} on CRW water with Pure Water

The water quality constituents such as (bi)-carbonate, DOC, tert-butanol and ammonia react with HO^\bullet and, therefore, affect O_3 decomposition and HO^\bullet concentrations during ozonation process. Figure 4.10 shows the effects of (bi)carbonate alkalinity (sum of bicarbonate and carbonate), DOC, ammonia and combination of (bi)carbonate alkalinity plus t-butanol on slow-stage R_{CT} at pH 6 and 8. In general, the values of R_{CT} increase one to two orders of magnitude when pH increases from 6 to 8. The constituents of (bi)carbonate alkalinity, DOC and/or t-butanol serve as good HO^\bullet scavengers, and thus R_{CT} decreases.

However, DOC also quickly reacts with O₃ and thus the change of R_{CT} by the addition of DOC is not as significant as compared to addition of (bi)carbonate alkalinity or t-butanol. Ammonia at the concentration of 0.5 mg-N/L has no effect on R_{CT} at pH 6 and 8. However, the reaction of O₃ with ammonia could become significant and thus increasing R_{CT} when increasing ammonia dose to a concentration of greater than 0.5 mg-N/L (data not shown). The results show that the order of scavenging HO[•] capability is t-butanol > (bi)carbonate alkalinity > DOC > ammonia at both pH 6 and 8. In comparison with pure water and CRW water, both fast- and slow-stage of R_{CT} for pure water is approximately five times higher than CRW water at pH 6, whereas a 80-fold higher for fast-stage and a 40-fold higher for slow-stage at pH 8. Figure 4.11 shows that, in general, with the same O₃ exposure, when water pH increases from 6 to 8, the calculated HO[•] exposure increases by two orders of magnitude for pure water, whereas less than an order of magnitude increase for the CRW water.

An experimental matrix was employed to examine the influence of water quality parameters and treatment variables on R_{CT} in CRW water by independently varying one parameter at a time from a set of baseline conditions (i.e., O₃ (initial): 3 mg/L, Br⁻: 170 µg/L, pH 7.5, temperature: 24 °C, (bi)carbonate alkalinity_(ambient): 1mM, DOC_(ambient): 3 mg/L). Experiments considering the effect of DOC that a higher initial O₃ concentration (4.5 mg/L) was applied. Typically, with the initial concentration of O₃ at 3 mg/L (6.25×10^{-5} moles/L), the values of R_{CT} are within the range between 10^{-7} to 10^{-9} , which resulting in the HO[•] concentrations are on the order of 10^{-12} to 10^{-14} moles per liter (M). Figures 4.12-4.17 show two-stage R_{CT} values on each set of experimental condition for different water quality parameters.

For the effect of bromide, the values of R_{CT} decreased from 3.2×10^{-8} to 1.0×10^{-8} for the fast stage and decreased from 1.3×10^{-8} to 4.4×10^{-9} for the slow stage, respectively as bromide levels increase from ambient 70 µg/L up to 470 µg/L (Figure 4.12). Increasing water pH from 6.5 to 8.5, the values of R_{CT} increased from 6.3×10^{-9} to 3.6×10^{-8} for fast stage and increased from 3.9×10^{-9} to 1.7×10^{-8} for the slow stage (Figure 4.13). The temperature also has a positive effect on R_{CT} value. As water temperature increases from 5 to 24 °C, the values of R_{CT} increased from 6.2×10^{-9} to 2.1×10^{-8} for the fast stage and gradually increased from 2.2×10^{-9} to 5.8×10^{-9} for the slow stage, respectively (Figure 4.14). The effect of (bi)carbonate alkalinity results (see Figure 4.15) show that the values of R_{CT} decreased from 4.7×10^{-8} to 2.0×10^{-8} for the fast stage and decreased from 2.5×10^{-8} to 8.5×10^{-9} for the slow stage, respectively as the

concentrations of (bi)carbonate alkalinity increases from 0.25 to 2 mM. Since the ambient DOC concentration in CRW was 3 mg/L, in order to check the effect of DOC on R_{CT} , additional amount of DOC was added into water to increase the desired different DOC concentrations. When conducting the effect of DOC experiments, higher initial O_3 concentration (4.5 mg/L) was employed to make sure that some O_3 residuals at 20 minutes still remain. As the concentration of DOC increased from 3 to 4.5 mg/L, the values of R_{CT} for the fast stage increase from 1.3×10^{-8} to 2.4×10^{-8} and gradually increased from 5.3×10^{-9} to 1.1×10^{-8} for the slow stage, respectively (Figure 4.16).

In general, R_{CT} values at fast stage are higher than at slow stage by a factor of 2 to 3. The values of R_{CT} decrease as increasing of water bromide and (bi)carbonate alkalinity levels, whereas increasing pH, temperature, and DOC resulting in increasing R_{CT} . With the R_{CT} value on each set of ozonation experiment, calculated HO^\bullet concentration or exposures can be obtained at any particular time by multiplying with O_3 residuals.

Considering the effect of treatment variables on R_{CT} , different O_3 doses, reaction times (exposure), pH depression, and ammonia addition were considered. In batch kinetic experiments, R_{CT} remains constant in each stage and is independent of the reaction time, while the accumulated O_3 exposures increase over time and increase as increasing initial O_3 concentrations. The values of R_{CT} decrease by a factor of between 2 and 3 for both fast and slow stages as initial O_3 concentrations increase from 2 to 4 mg/L (Figure 4.17).

In order to reduce unwanted bromate formation, typically adding acid and/or ammonia are the two most common methods for controlling the formation of bromate. As described above, the values of R_{CT} will decrease when acid is added into water due to higher O_3 remaining and less HO^\bullet formation at lower pH. Another alternative of reducing bromate formation is by adding small amount of ammonia. Based upon the molar ratio of bromide and ammonia concentration (molar ratio of $\text{NH}_4^+/\text{Br}^-$) from 0 to 60 for various experiments, different doses (0-1.8 mg-N/L) of ammonia were added into water before ozonation. The results show that when the molar ratio of $\text{NH}_4^+/\text{Br}^-$ is less than 30 ($\text{NH}_4^+ = 0.45 \text{ mg-N/L}$), the O_3 decomposition rates and the values of R_{CT} were not affected (Table 4.1). However, when addition of ammonia is much greater than 1.0 mg-N/L, O_3 decomposition rates and R_{CT} started slightly increased.

12.3.4. 4.3.4 Bench-Scale continuous flow ozonation:

During bench-scale continuous-flow ozonation, applied ozone dose was remained constant. Experiments with different hydraulic retention times (HRTs=V/Q), pH depression and various amounts of ammonia addition were conducted. Based on the profiles of O₃ residuals and PCBA concentrations at various ports in which representing different hydraulic retention times, values of R_{CT} were calculated by plotting logarithm of [PCBA]_t/[PCBA]₀ versus ozone exposure ([O₃]_{residual}×HRT). As water flows decreased, O₃ residuals remained higher, but the values of R_{CT} decreased. Table 4.2 shows that when the flow decreased from 0.51 L/min to 0.14 L/min, the HRTs at the first port (Port 1) increased from 1.9 to 6.9 minutes and the O₃ residuals increased from 0.41 to 1.1 mg/L and the R_{CT} values decreased from approximately 8.1×10^{-8} to 1.8×10^{-8} , respectively, which fall on the same orders of magnitude as batch ozonation.

Figure 4.18 shows ozone residuals and HO[•] concentrations profiles in ozonation at different water flow rates. As expected, O₃ residual in each port increased as decreasing water flow rate, which resulting in grater applied O₃ dose. However, the calculated concentrations of HO[•] decreased when lower flow rates were applied, even though O₃ residuals remained higher. The is due to that increasing water flow leaded to decreasing HTR at each port and therefore, decreased the applied O₃ doses and shifted ozonation reaction towards to fast stage.

Table 4.2 shows the addition of acid resulted in increase of O₃ residuals from 0.98 to 1.2 mg/L when the water pH was depressed from 8.2 to 7.0 and decreased R_{CT} from 2.3×10^{-8} to 1.7×10^{-8} , approximately 30% of reduction. For the second set of continuous flow experiments, different ammonia doses were added to 25 liters of CRW water to adjust the molar ratio of NH₄⁺/Br⁻ (from 0 to 10) while maintaining water flow at 0.2 L/min prior to ozonation. Table 4.3 shows that O₃ residuals, values of R_{CT} and HO[•] concentrations did not vary by the addition of ammonia dose of less than 0.4 mg-N/L. However, when ammonia concentration increased to 0.4 mg-N/L, R_{CT} and HO[•] concentrations slightly increased due to the O₃ reaction with ammonia become important.

12.3.5. 4.3.5 Pilot-scale continuous flow ozonation:

Some pilot-scale continuous flow ozonation experiments were conducted using the pilot unit operated by Carollo Engineers at Union Hills Water Treatment Plant in Phoenix, Arizona, where CRW is used as source water. O_3 doses were controlled to simulate the same kinetic ozone decomposition conducted in batch ozonation experiments (O_3 (initial)= 3 mg/L) for the three types of water qualities used in this task, which are the CRW water, the CRW water plus ammonia addition with the molar ratio of NH_4^+ / Br^- equals to 3 and the CRW water plus 16 mg/L of $FeCl_3$ & 0.35 mg/L of C_3O_8P polymer addition. The R_{CT} values were calculated using the same approach as bench-scale continuous flow experiments. Table 4.4 shows the experimental conditions and values of R_{CT} in both pilot and batch ozonation experiments. For the water in ambient conditions and water with ammonia addition experiments, kinetic O_3 decay curves were similar and the values of R_{CT} for pilot ozonation tests are almost the same as for batch experiments. For water with pretreatment of coagulant ($FeCl_3$ and polymer) experiments initially used the same O_3 dose (1.9%) as for the first two tests, ozone residuals were almost two-fold higher than the first two tests. This is because that the water pH was depressed by approximately 1 unit (from 8.2-7.3) and turbidity was reduced (from 0.9 to 0.3 NTU.) after treatment of coagulant. Therefore, ozone dose was reduced down to 1.14% to maintain similar O_3 residuals to the previous two experiments and thus the R_{CT} decreased down to 8.0×10^{-9} . Further lowering O_3 dose down to 0.65% resulted in decrease of O_3 residuals and increase of R_{CT} to 1.5×10^{-8} . Using the same coagulant treated water for the batch experiment shows that the ozone decay curve was within the range of the two pilot curves, which explains why the value of R_{CT} is (1.1×10^{-8}) between the values (8.0×10^{-9} and 1.5×10^{-8}) from pilot experiments.

12.4. 4.4 DISCUSSION

In batch ozonation experiments, a three-stage ozone decomposition processes were observed. First, instantaneous ozone demand (IOD) occurred as soon as an aliquot of a stock O_3 solution is added. This agrees with Park et al (2001) approach on measuring IOD and its definition: the difference between administered ozone and the amount of ozone measured after a few seconds. Kinetically, a turning point occurred at approximately 2 minutes on first-order O_3 decomposition plot (see Figure 4.7). In addition, the two separate kinetic stages are also revealed in the corresponding R_{CT} plot. Because of rapid O_3

decomposition in the fast stage, it is difficult to acquire sufficient and accurate enough kinetic to well quantify the R_{CT} at fast stage. However, good linear interpretation of R_{CT} for both the fast and slow-stage provides a useful tool to empirically determine HO^{\bullet} concentration from known O_3 measurements.

In general, R_{CT} varies as change of water quality and/or treatment variables. However, once a comprehensive database of R_{CT} values for a single water source is developed, O_3 as well as HO^{\bullet} concentrations can be predicted based upon the water quality and treatment conditions throughout the whole ozonation process. This will be very helpful in terms of controlling efficiency of disinfection and DBP formation. Up to now, databases of O_3 decomposition under different water quality and treatment conditions have been well developed. However, kinetics of HO^{\bullet} during ozonation are still predicted by kinetic models and calibration is always needed when predicting HO^{\bullet} concentrations. Usage of empirical measurement for HO^{\bullet} , therefore, can provide more reliable and accurate information on changes of HO^{\bullet} concentration throughout an ozonation process.

As efficiency of microorganism inactivation is always defined as O_3 exposure (or CT, expressed as product of O_3 concentration and contact time), HO^{\bullet} exposure is somewhat important in terms of micropollutant removal. Figures 4.19-4.24 show HO^{\bullet} exposure with respect to its O_3 exposure for in a given water under given reaction conditions. Effects of each individual water quality parameter and treatment condition are discussed below:

12.4.1. 4.4.1 Effect of Water Quality Parameters on R_{CT}

4.4.1.1 Effect of Br^-

Bromide ion reacts with both molecular O_3 and its decomposition by-product, HO^{\bullet} , radicals and thus can influence ozone decomposition rate. Oxidation reactions of Br^- by these two oxidants are very complicated that contain a series of chain reactions that involve different bromine and bromine radical species as intermediates (von Gunten and Hoigne, 1994). In general, bromide ions can react with O_3 and HO^{\bullet} that can consume O_3 on one hand, and, meanwhile, prevent O_3 from decomposition by scavenging HO^{\bullet} on the other hand. Figure 4.19 is a plot showing the relationship of HO^{\bullet} exposure versus O_3 exposure at different bromide levels. HO^{\bullet} exposures decrease as increasing Br^- levels at the same O_3 exposures.

However, from O_3 exposure standpoint, more O_3 dose needs to be introduced to achieve the same level of HO^\bullet exposure as water bromide level increases.

4.4.1.2 Effect of pH

Hydroxide ions (OH^-) initiate O_3 decomposition and control HO^\bullet formation. Increasing pH means more hydroxide ions (OH^-) react with O_3 and thus producing more HO^\bullet in a fixed time interval. Since HO^\bullet is involved in chain decomposition of O_3 , increasing HO^\bullet concentrations result in increase of O_3 decomposition. This implies the R_{CT} could strongly be affected by water pH. Figure 4.20 shows the relationship of HO^\bullet exposure versus O_3 exposure at different pH levels. HO^\bullet exposures increase rapidly as increasing pH when applying the same O_3 exposures. The negative impact on O_3 exposure and positive impact on HO^\bullet exposure by pH results in a consequence of the ca. 6-fold and 4-fold increase when water pH increases from 6.5 to 8.5.

4.4.1.3 Effect of temperature

As expected, ozone decomposition rates increase as increasing temperature due to kinetic and thermodynamic factors. Figure 4.21 shows that for the same experimental conditions, O_3 exposures at any particular time decrease as increasing water temperature, while HO^\bullet exposure as water temperature increases. These positive effects of temperature on increasing R_{CT} result in 3-fold increase when temperature increases from 5 to 24 °C.

4.4.1.4 Effect of (Bi)carbonate Alkalinity

The effects of (bi)carbonate alkalinity on R_{CT} are major from its reaction with HO^\bullet . According to the definition of alkalinity (Alkalinity= $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [H^+]$), the effect of alkalinity can be related to the effects of total inorganic carbon (TIC) at constant pH value. During ozonation process, O_3

does not react with carbonate species. However, carbonate and bicarbonate act as HO[•] scavengers (Buxton et al., 1988) and therefore, stabilize aqueous O₃ decomposition by the following reactions:



Typically natural source waters' pH ranges from 6-9, thus the (bi)carbonate alkalinity is major from bicarbonate species. Figure 4.22 shows that for the same O₃ exposures, HO[•] exposure decreases as increasing the amount of TIC.

4.4.1.5 Effect of DOC

When NOM is present in waters, NOM predominately behaves as a direct consumer of ozone (Westerhoff, et al. 1997). In addition, NOM may act as initiators, promoters and inhibitors of the HO[•] chain reactions (Park et al., 2001). The amount of NOM existing in waters can be expressed as DOC and affects the O₃ consumption and HO[•] strongly during ozonation of natural waters. Figure 4.23 shows that when O₃ exposure remains unchanged, the concentrations of HO[•] increase as DOC concentration of CRW water increases.

4.4.1.6 Effect of treatment variables on R_{CT}

Different water quality conditions show the rates of O₃ decomposition are different. In addition, ozonation treatment variables such as applied initial O₃ dose, reaction time, pH depression and ammonia addition may also affect the R_{CT}. Details will be discussed as follows:

4.4.1.7 Effect of ozone doses and contact time

Both ozone dose and contact time can affect R_{CT} value. Figure 4.24 shows that as increasing initial ozone dose, values of R_{CT} slightly decrease due to more stable of ozone decomposition that increases

ozone residual half-life at higher ozone concentrations (data not shown). On the other hand, a fast stage of ozonation occurs within to 2 minutes as soon as ozone is added and then followed by a slower stage of ozonation, which implies ozone depletion and HO[•] generation are a function of reaction time. In the presence of NOM in water, ozone can rapidly react with NOM and form HO[•]. Since NOM is a mixture of heterogeneous organic carbons, a very rapid ozone reaction with active organic sites occurs immediately followed by reacting with slower organic sites. This could, therefore, explain that higher ozone doses results in higher over HO[•] concentrations in CRW water even when at the point of the same ozone exposure.

4.4.1.8 Ammonia addition

The reaction rates of O₃ and HO[•] with ammonia is normally much slower than with other organic and/or inorganic compounds. Therefore ammonia addition doesn't affect R_{CT}, which means that O₃ as well as HO[•] concentrations during ozonation are not affected by the addition of ammonia.

In general, effects of individual water quality parameter on O₃ exposure, R_{CT} as well as HO[•] exposure show trends that most water quality parameters have negative impact on O₃ exposure except (bi)carbonate alkalinity. Water quality parameters such as pH, temperature and DOC have positive influence on R_{CT} and negative impact for bromide and (bi)carbonate alkalinity. These results in the HO[•] exposure increase as water pH, temperature and DOC increase, but decreases as bromide and (bi)carbonate alkalinity increase.

12.4.2. 4.4.2 Comparison of R_{CT} between bench- and pilot-scale ozonation

When ozone decay kinetics are similar, the value of R_{CT} is not affected by water hydraulics when applying the same water quality and ozone treatment conditions. Figure 4.25 shows that the values of R_{CT} remain the same in both bench-scale batch and pilot continuous ozonation processes using the same water quality and treatment processes (e.g., applying the same O₃ dose to obtain the same O₃ residuals.) for waters with and without ammonia addition. Table 4.4 shows the values of R_{CT} in pilot continuous flow and batch ozonation experiments under different water quality and treatment conditions. The hydraulics seems

does not affect the ratio of HO[•] and O₃ concentrations throughout the process. However, this only applies for the slow stage of ozonation. The fast stage of R_{CT} for continuous flow ozonation could not be determined due to unavailability of O₃ residual and HO[•] concentration profiles in the process. When the water quality is changed by addition of coagulants, both water pH and turbidity decrease. Therefore, the R_{CT} decreases as a result of increasing ozone residuals (Table 4.4). The difference of R_{CT} in batch and pilot ozonation of water with coagulant addition is because the difference of O₃ residual profiles. Overall O₃ dose is probably key of controlling R_{CT} since it is a function of the required O₃ residual, the ozone key kinetics.

12.5. 4.5 CONCLUSIONS

In this study, bench-scale batch and continuous flow and pilot-scale kinetic ozonation varied the reaction individual parameters for examining effect of various water quality conditions and treatment variables on O₃ and HO[•] concentrations were investigated. The following conclusions were withdrawn from the results:

- By adding trace amount of PCBA into water, the concentrations of HO[•] formation during ozonation process can be determined by the product of O₃ concentration and R_{CT}.
- Ozonation of water with a set of water quality and treatment condition, a two-stage R_{CT} was defined, which is a fast stage followed by a slow stage.
- The values of R_{CT} are affected by water quality parameters. In general, R_{CT} values during the fast stage (0-2 minutes) are higher than during the slow stage (> 2minutes) by a factor of 2 to 3. The values of R_{CT} increase proportionally with increasing water pH, temperature, and concentration of DOC and decrease proportionally with increasing bromide and (bi)carbonate alkalinity levels (Table 4.6 and Table 4.7).
- The values of R_{CT} for ozonation of CRW water are within the range between 10⁻⁷ to 10⁻⁹, which resulting in the HO[•] concentrations are on the order of 10⁻¹² to 10⁻¹⁴ moles per liter (M).
- For addition of ammonia at the concentrations of less than 0.5 mg-N/L, R_{CT} remains constant for both bench and pilot-scale ozonation with the same treatment conditions.

- The value of R_{CT} is not affected by water hydraulics as long as applying the same water quality and ozone treatment conditions. The results of batch and pilot-scale continuous flow experiments show that under the same water quality and ozone dose, the value of R_{CT} is on the order of 1.8×10^{-8} .
- Once the R_{CT} database has been developed for any particular source water, the concentrations of O_3 and HO^\bullet can be determined, and therefore the ability of disinfection/oxidation as well as formation of DBPs could be monitored.

12.6. REFERENCES

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Table 4.1 - Values of R_{CT} in batch ozonation experiments at various pH and ammonia dosages (conditions: O_3 : 3 mg/L, Br^- : 170 μ g/L, temperature: 24 °C)

NH_4^+/Br^- (molar ratio)		$R_{CT} (\times 10^8)$ (0-2 minutes)	$R_{CT} (\times 10^8)$ (2-20 minutes)
pH 6.5	0-30	0.8±0.01	0.5±0.08
pH 7.5		1.8±0.1	0.8±0.09
pH 8.5		3.0±0.3	1.5±0.1
pH 6.5		0.9	0.6
pH 7.5	60	2.1	1.0
pH 8.5		3.5	1.8

Table 4.2- Values of R_{CT} , O_3 residuals and HO^\bullet calculated concentrations in bench-scale continuous flow ozonation of various HRTs, and acid or ammonia addition ($V_{overall} = 2.5L$).

Exp. No.	Flow (Q) (L/min)	HRT (V/Q) (minutes)			$R_{CT} (\times 10^8)$
		Port 1	Port 2	Port 3	
1	0.51	1.9	3.9	4.9	8.1
2	0.43	2.2	4.6	5.8	5.0
3	0.26	3.7	7.6	9.6	2.7
4	0.20	4.4	9.0	11.3	2.3
5	0.14	6.9	14	17.8	1.8
6 ^a	0.20	4.4	9.0	11.3	1.7
7 ^b	0.20	4.4	9.0	11.3	2.4

^a pH depression experiment (from pH 8.2 to 7.0); ^b ammonia addition experiment (NH_4^+/Br^- molar ratio=3).

Table 4.3- Values of R_{CT} , O_3 residuals and calculated HO^\bullet concentrations in bench-scale continuous flow ozonation of various doses of ammonia addition

Exp. No.	Ammonia addition in μ g/L (NH_4^+/Br^- in molar ratio)	$R_{CT} (\times 10^8)$	O_3 residual (mg/L)	HO^\bullet concentration (M)
1	0 (0)	2.5	1.01	5.2×10^{-13}
2	40 (1)	2.5	0.99	5.2×10^{-13}
3	40 (1)	2.5	0.99	5.2×10^{-13}
4	120 (3)	2.5	0.98	5.2×10^{-13}
5	400 (10)	2.8	0.92	5.3×10^{-13}

Table 4.4- Values of R_{CT} in pilot and batch ozonation experiments

Pilot Plant Treatment Conditions	$R_{CT} (\times 10^8)$	Batch Treatment Conditions	$R_{CT} (\times 10^8)$
Ambient water O_3 : 1.9%	1.8	Ambient O_3 (initial): 3 mg/L	1.8
Ammonia (NH_4^+ /Br ⁻ : 3) O_3 : 1.9%	1.8	Ammonia (NH_4^+ /Br ⁻ : 3) O_3 (initial): 3 mg/L	2.1
Coagulant addition (16 mg/L $FeCl_3$ & 0.35 mg/L C_3O_8P polymer) O_3 : 1.14%	0.8	Coagulant addition (16 mg/L $FeCl_3$ & 0.35 mg/L C_3O_8P polymer) O_3 : 3 mg/L	1.1
Coagulant addition (16 mg/L $FeCl_3$ & 0.35 mg/L C_3O_8P polymer) O_3 : 0.65%	1.5		

Table 4.5- Effect of water quality parameters on O₃ exposure, R_{CT} values and HO[•] exposure for CRW water ozonation (baseline conditions: Q₃: 3 mg/L; Br⁻: 170 µg/L; pH 7.5; temperature: 24 °C; (bi)carbonate alkalinity: 2mM; DOC: 3 mg/L, time: 20 min, Q₃: 4.5 mg/L for DOM experiments).

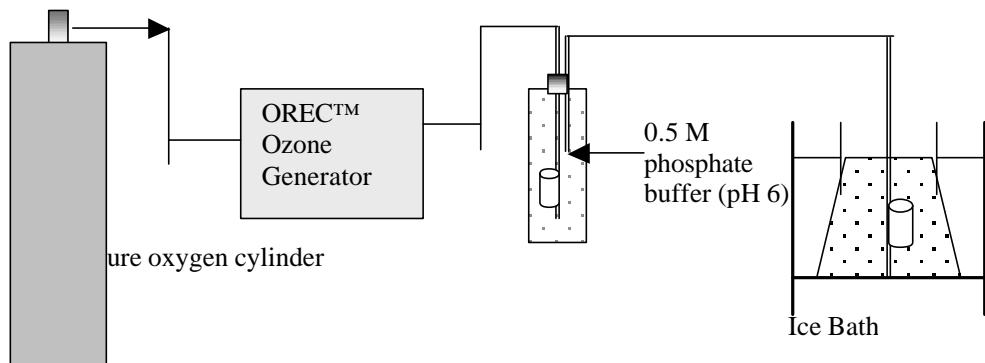
Parameters	Values	O ₃ -CT, Fast ($\times 10^5$)	HO [•] -CT, Fast ($\times 10^{12}$)	O ₃ -CT, Overall ($\times 10^5$)	HO [•] -CT, Overall ($\times 10^{12}$)
		Units	(M-min)	(M-min)	(M-min)
Bromide	70		7.9	2.2	35
	170	µg/L	7.3	1.5	32
	320		7.1	0.9	30
	470		6.8	0.6	28
pH	6.5		8.6	0.5	52
	7.5	---	7.9	1.2	40
	8.2		6.9	1.8	27
	8.5		6.4	2.1	22
Temperature	5		10	0.5	72
	10	°C	8.8	0.7	56
	15		8.3	0.9	50
	24		7.8	1.4	37
Alkalinity	0.25		7.2	3.0	30
	0.5	mM	7.4	2.5	32
	1		7.8	2.1	34
	2		8.5	1.5	43
DOM	3		13	1.4	69
	3.5	°C	12	1.6	60
	4		11	1.9	52
	4.5		10	2.2	41

Table 4.6- Trends of O₃ exposure, R_{CT} and HO[•] exposure on water quality parameters during ozonation.

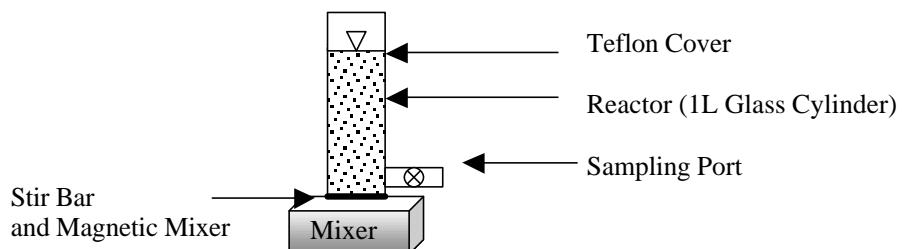
Parameters	Level	O ₃ -CT	R _{CT}	HO [•] -CT
pH	↑	↓	↑	↑↑
Temperature		↓	↑	↑
Bromide		↓	↓	↓↓
Alkalinity		↑	↓	↓↓
DOC		↓	↑	↑

Table 4.7- Relationships between water quality parameters and R_{CT} for batch ozonation.

Parameters	R ²		Referred Figure
	R _{CT} , fast	R _{CT} , slow	
Bromide	0.94	0.83	4.12
pH	0.99	0.98	4.13
Temperature	0.98	0.99	4.14
Alkalinity	0.98	0.93	4.15
DOC	0.99	1.00	4.16



(a) Stock ozonation generation system



(b) Batch ozonation reactor

Figure 4.1 - Schematic layout of (a) stock ozonation generation system and (b) batch ozonation reactor.

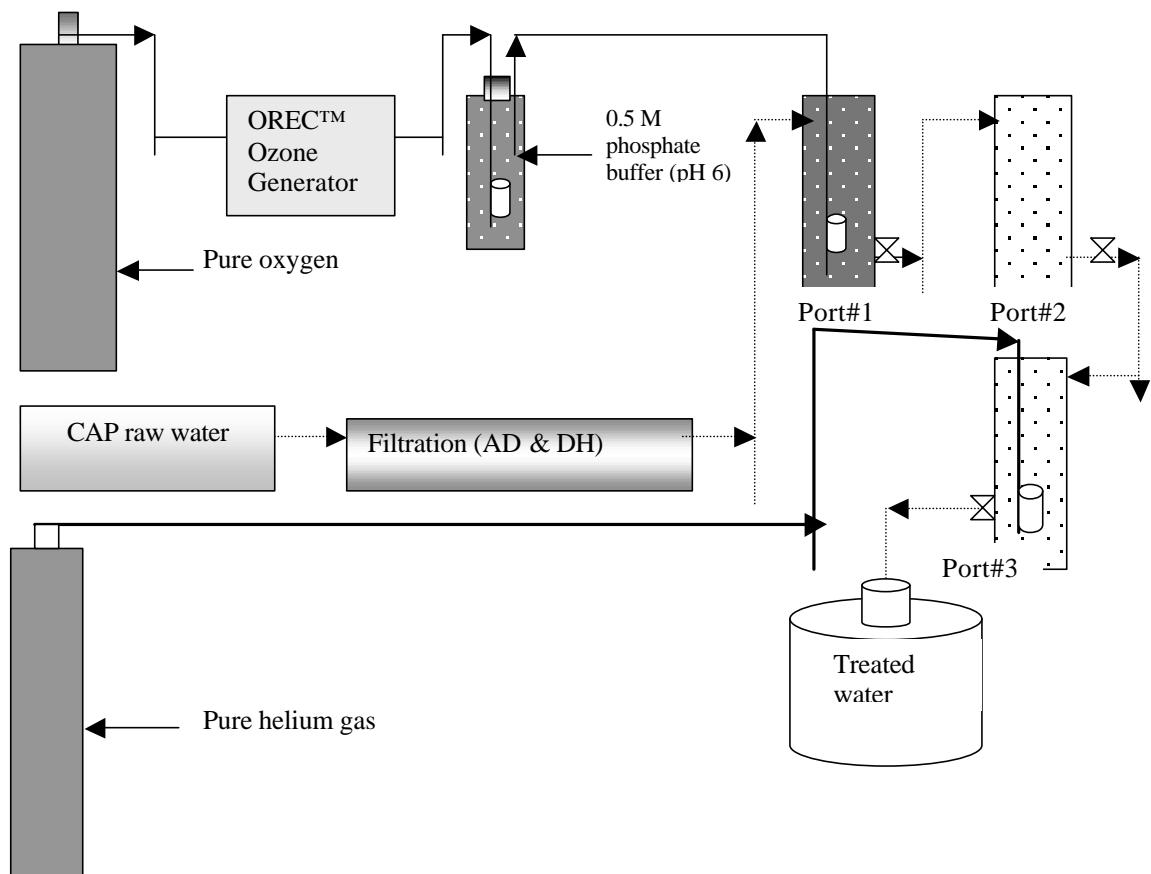


Figure 4.2- Schematic layout of continuous flow ozonation unit (dashed arrows represent water flows during continuous flow ozonation experiments)

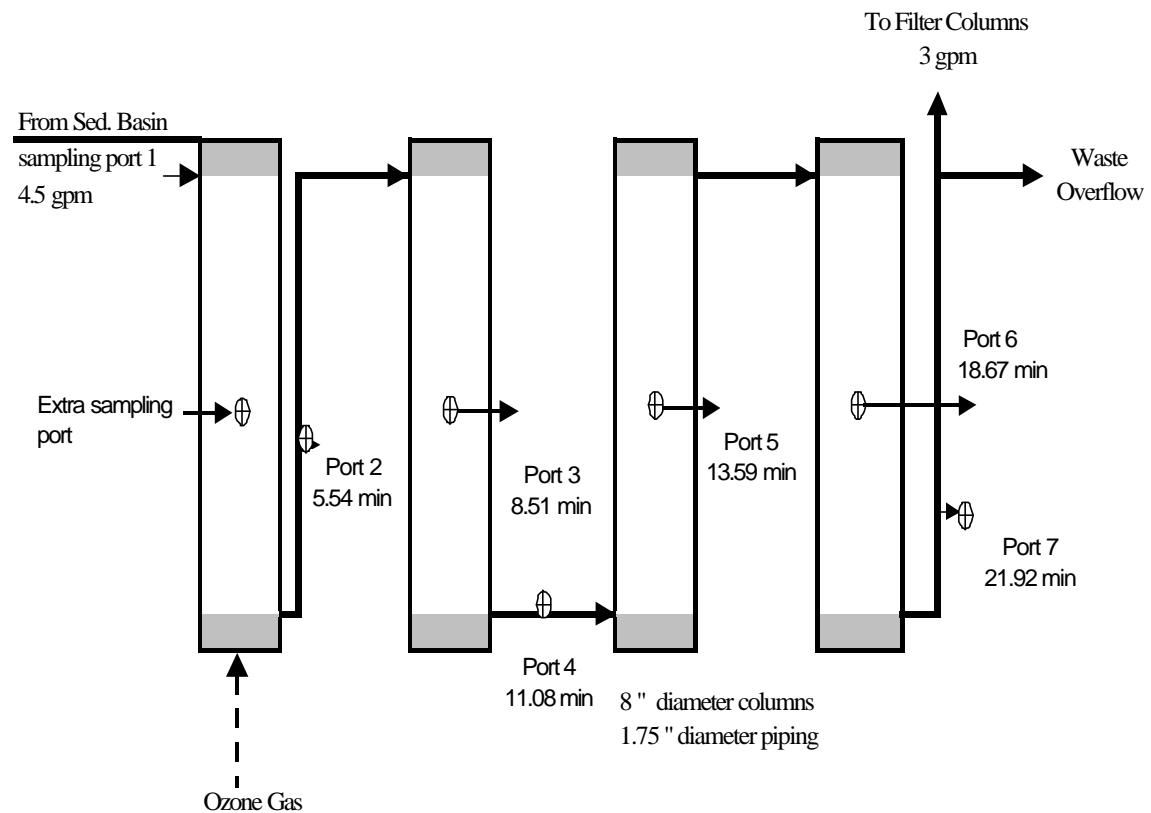


Figure 4.3- Pilot plant ozone contactor columns with sample port location and cumulative residence time.

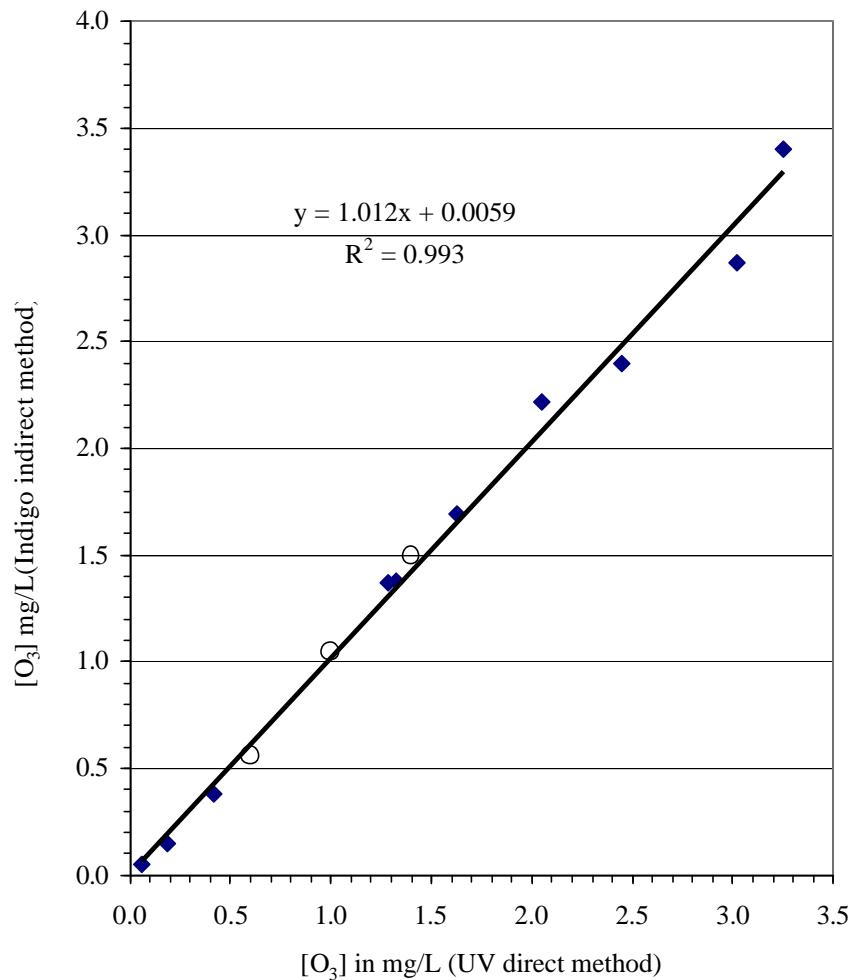


Figure 4.4- Comparison of Indigo/UVA method vs. direct UVA measurement of measuring dissolved ozone (opened circles represent values measured in ambient CRW water).

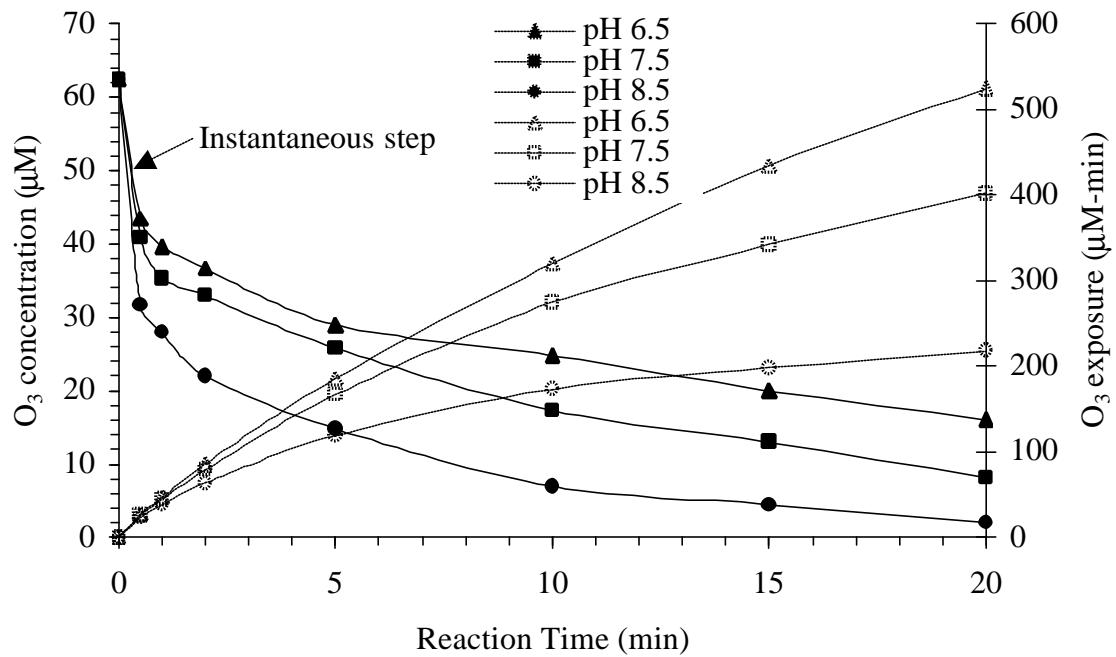


Figure 4.5- Ozone concentrations over time during ozonation at pH 6.5, 7.5 and 8.5
 (conditions: O₃= 3 mg/L, Br⁻= 170 μg/L, temperature 24 °C, Alk.=2 mM, DOC= 3mg/L).

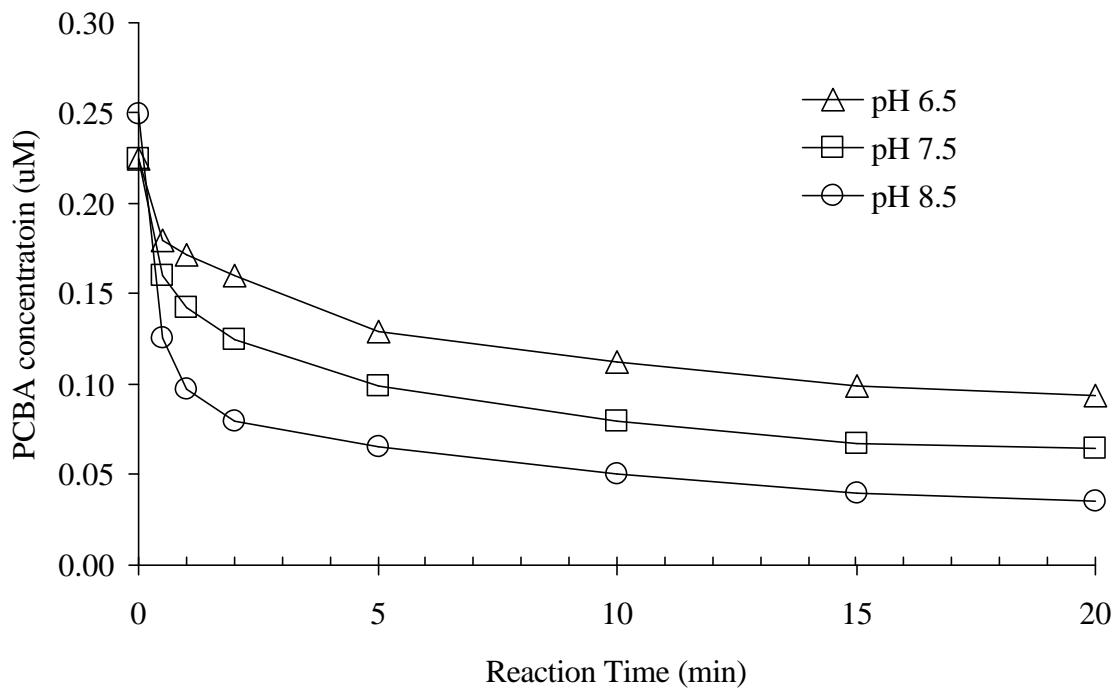


Figure 4.6- PCBA concentrations over time during ozonation at pH 6.5, 7.5 and 8.5
(conditions: $O_3= 3 \text{ mg/L}$, $Br^- = 170 \mu\text{g/L}$. temperature 24°C , Alk=2 mM, DOC= 3mg/L).

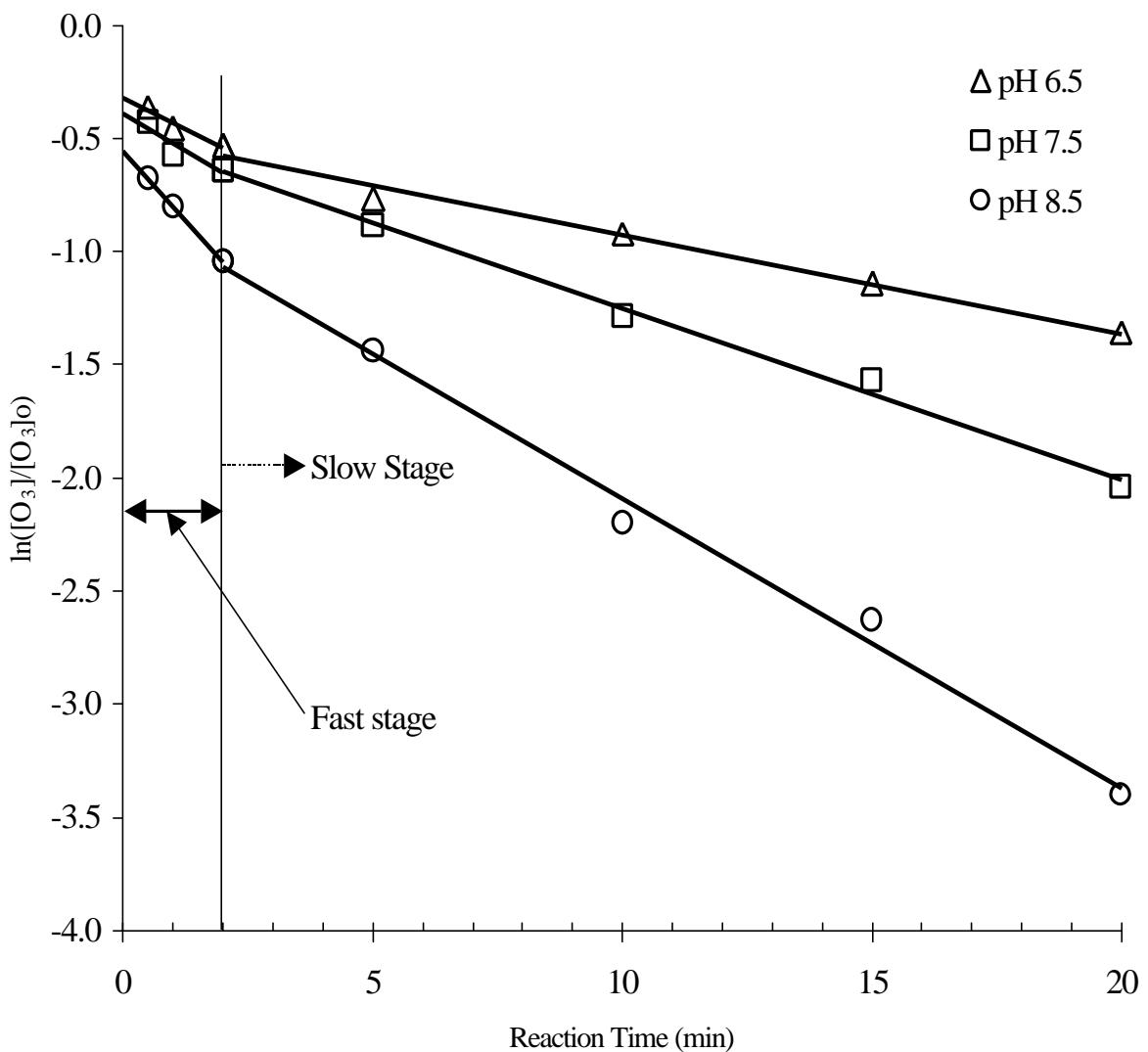


Figure 4.7 - First-order kinetics for O_3 depletion at pH 6.5, 7.5 and 8.5 (conditions: $O_3 = 3 \text{ mg/L}$, $Br^- = 170 \mu\text{g/L}$, temperature 24°C , Alk.=2 mM, DOC= 3mg/L)

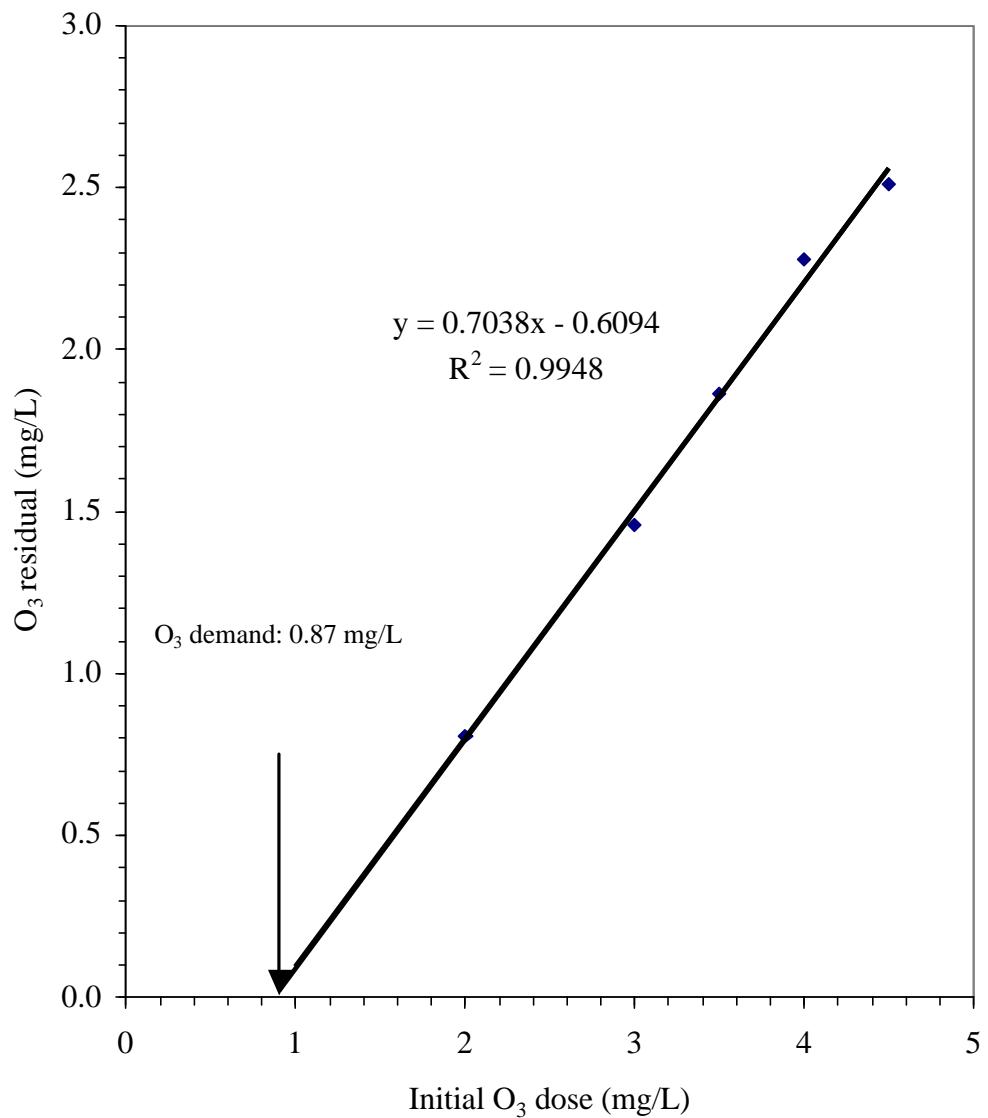


Figure 4.8- Raw CRW water ozone demand curve (conditions: temperature 24 °C and pH 7.5)

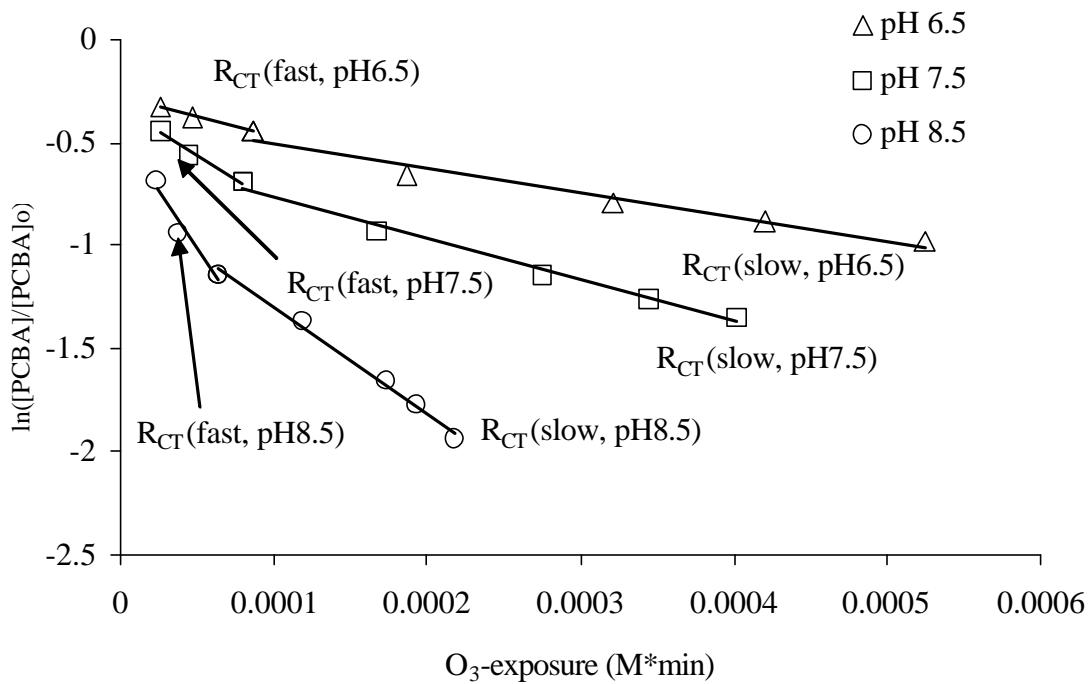


Figure 4.9- R_{CT} value calculations for ozonation at pH 6.5, 7.5 and 8.5 (conditions: $O_3=3\text{ mg/L}$, $Br^- = 170\text{ }\mu\text{g/L}$, temperature 24°C , Alk=2 mM, DOC= 3mg/L)

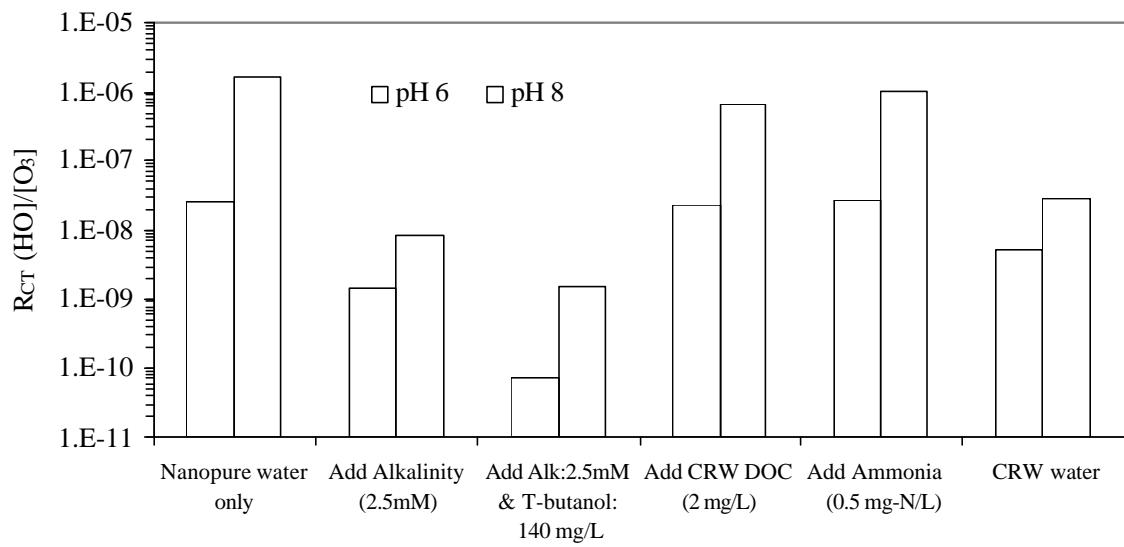


Figure 4.10- Effect of water quality parameters on R_{CT} for (Nano)pure water and raw CRW water during ozonation at pH 6 and 8 (conditions: $\text{O}_3= 2 \text{ mg/L}$, temperature 24°C).

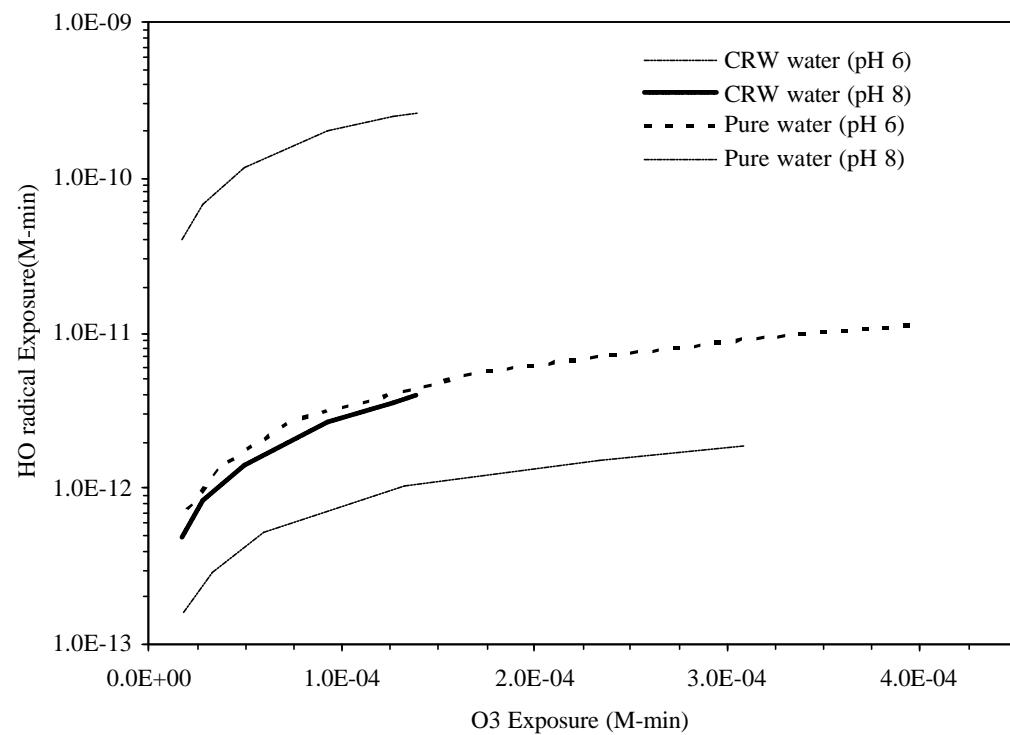


Figure 4.11- O₃ and HO[•] exposures during ozonation of (Nano)pure water and CRW water at pH 6 and 8 (conditions: O₃= 2 mg/L, temperature 24 °C).

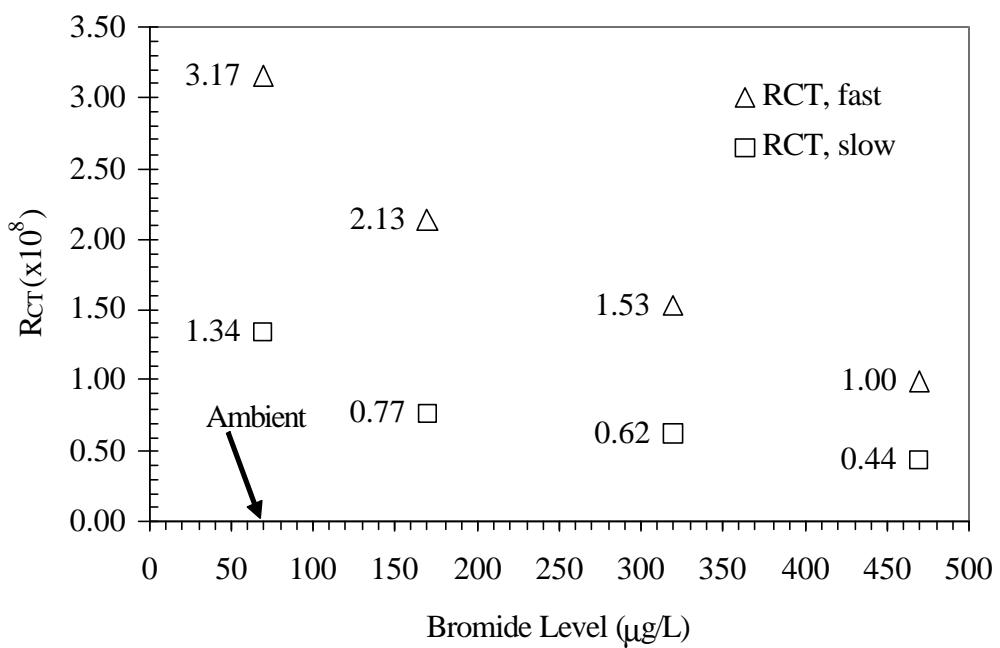


Figure 4.12- Effect of bromide level on R_{CT} values (conditions: $\text{O}_3= 3 \text{ mg/L}$, $\text{pH} = 7.5$, temperature 24°C , $\text{Alk.}=2 \text{ mM}$, $\text{DOC}= 3\text{mg/L}$).

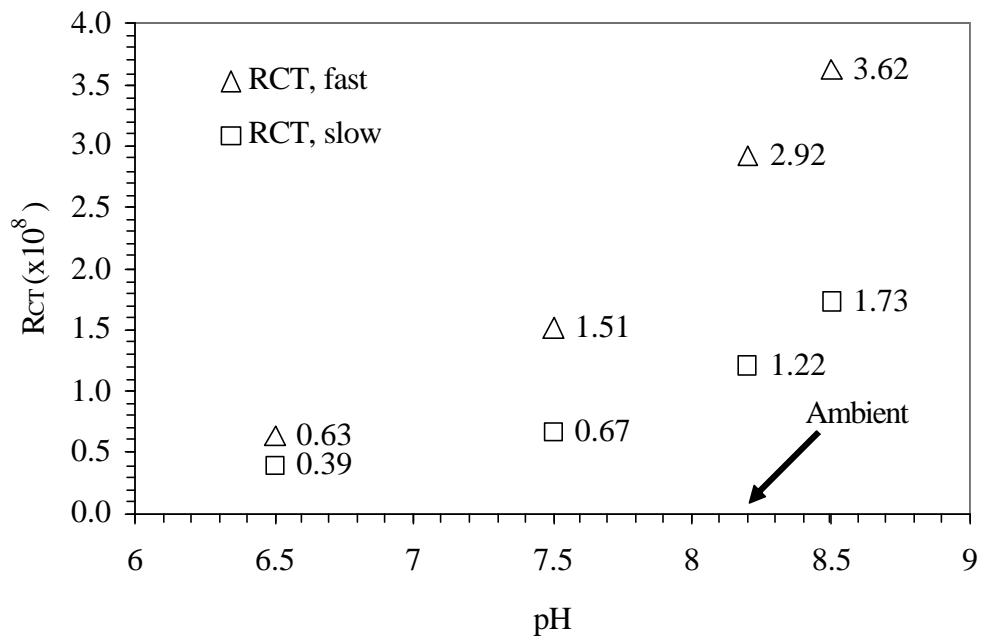


Figure 4.13- Effect of pH on R_{CT} values (conditions: $O_3= 3 \text{ mg/L}$, $Br^- = 170 \mu\text{g/L}$. temperature 24°C , Alk.=2 mM, DOC= 3mg/L).

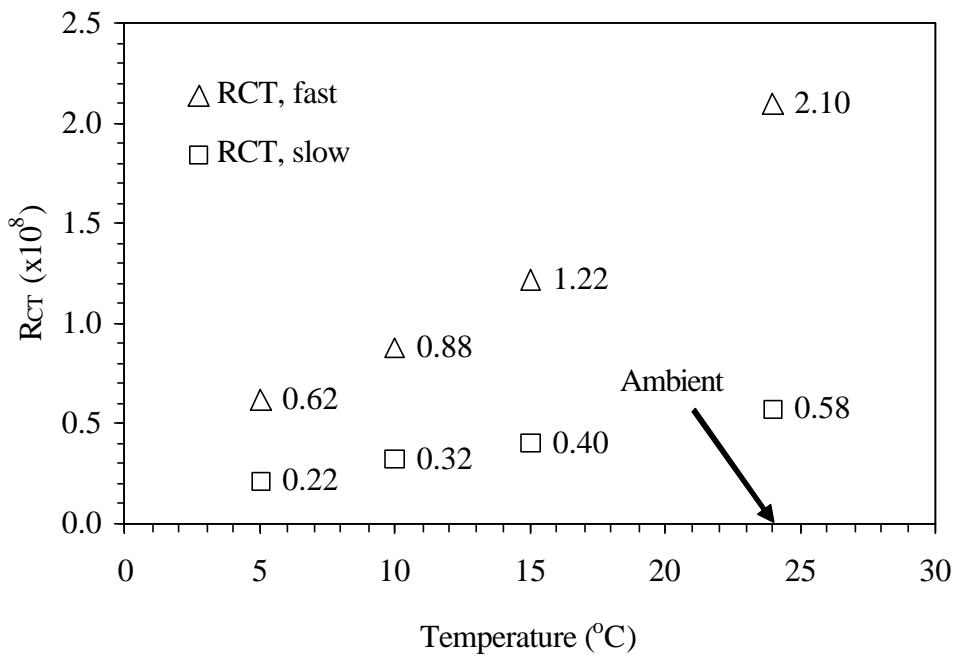


Figure 4.14- Effect of temperature on R_{CT} values (conditions: $\text{O}_3 = 3 \text{ mg/L}$, $\text{Br}^- = 170 \mu\text{g/L}$, $\text{pH} = 7.5$, $\text{Alk.} = 2 \text{ mM}$, $\text{DOC} = 3 \text{ mg/L}$).

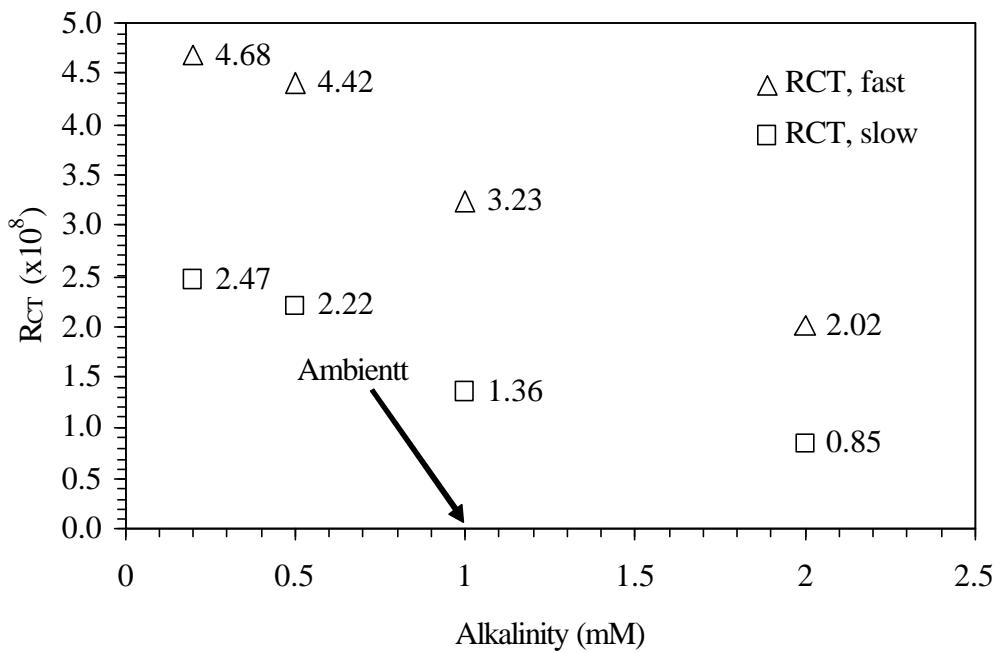


Figure 4.15- Effect of (bi)carbonate alkalinity on R_{CT} values (conditions: $O_3=3\text{ mg/L}$, $Br^- = 170\text{ }\mu\text{g/L}$. $pH = 7.5$, temperature 24°C , DOC= 3mg/L)

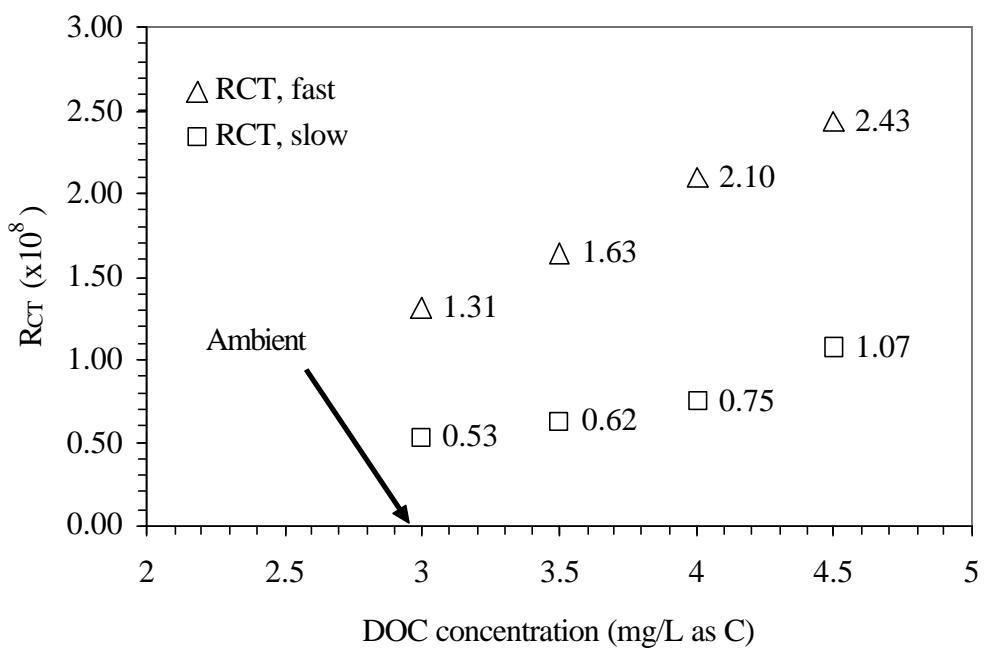


Figure 4.16- Effect of DOC concentration R_{CT} values (conditions: $O_3 = 3$ mg/L, $Br^- = 170$ μ g/L, $pH = 7.5$, temperature 24 °C, Alk.= 2 mM)

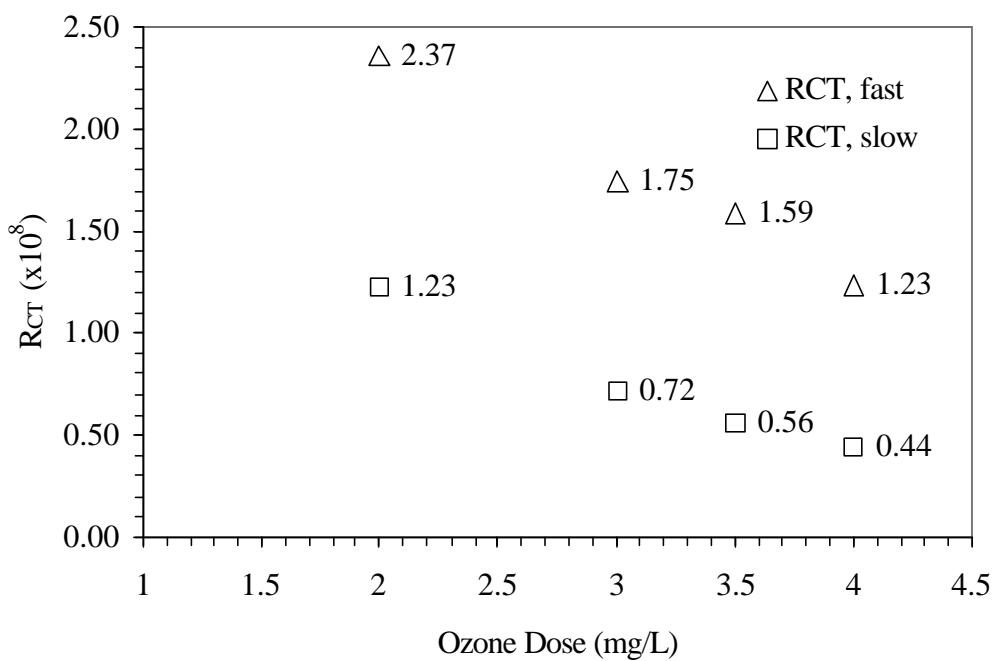


Figure 4.17- Effect of ozone concentration R_{CT} values (conditions: $Br^- = 170 \mu g/L$, $pH = 7.5$, temperature $24^\circ C$, $Alk. = 2 mM$, $DOC = 3 mg/L$).

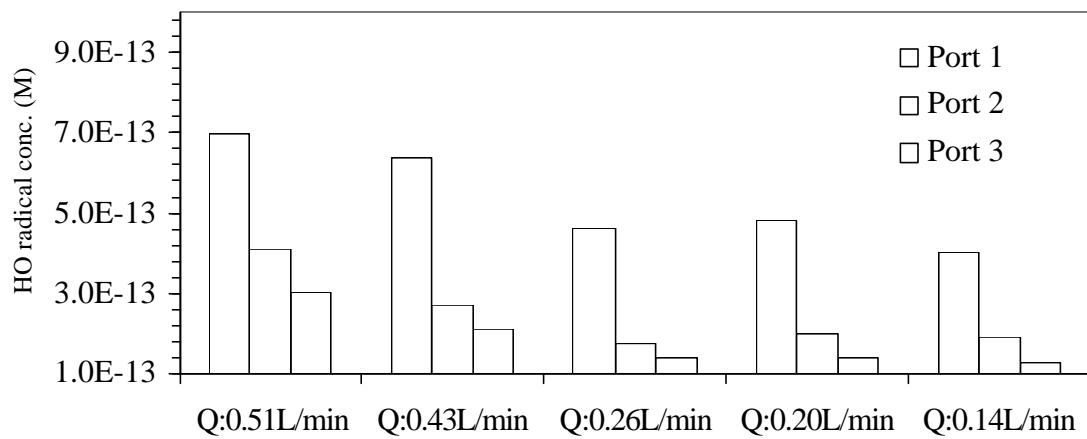
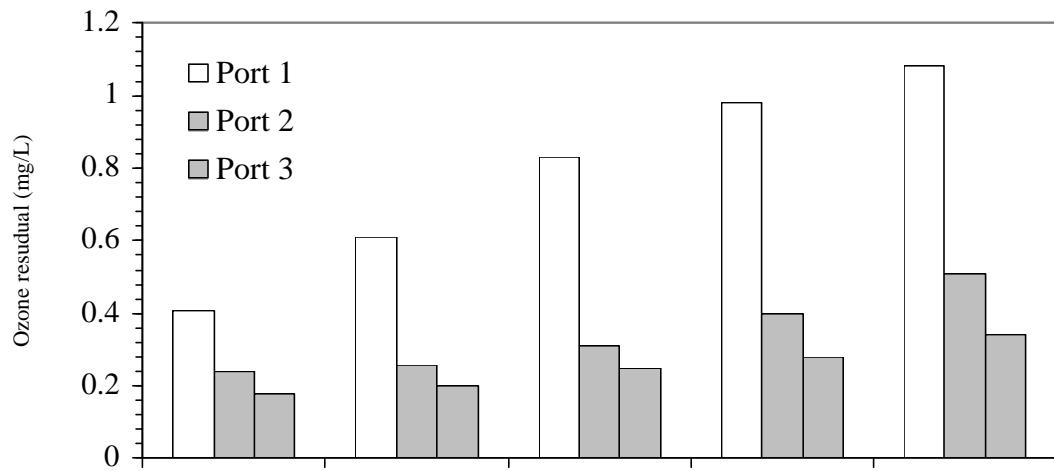


Figure 4.18- O_3 and HO^\bullet profiles in bench-scale continuous flow ozonation with various water flow rates.

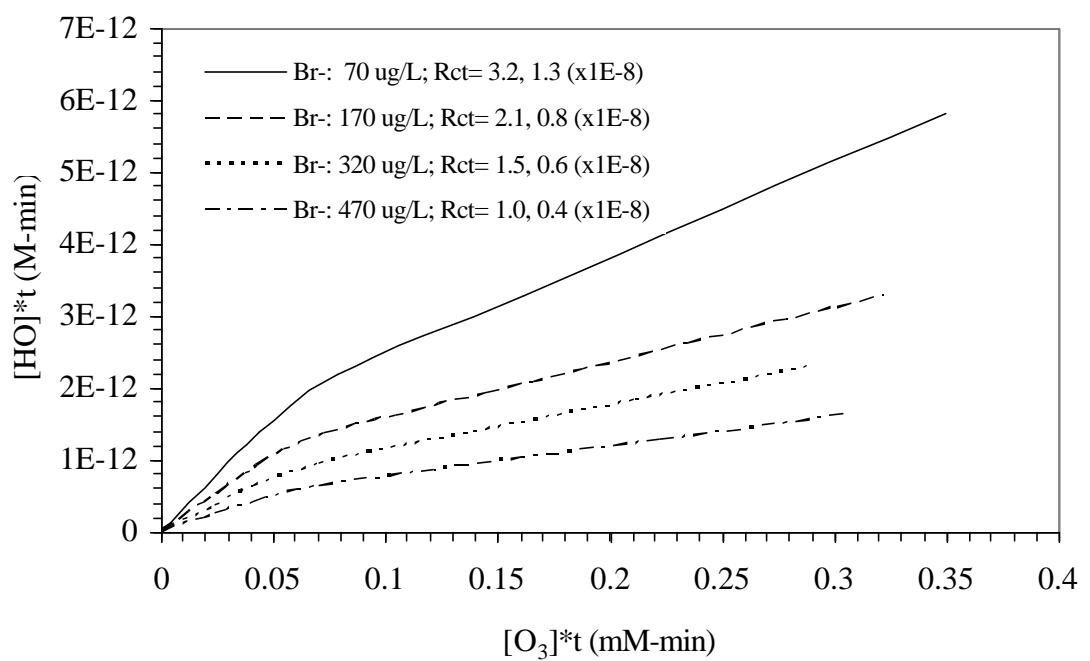


Figure 4.19- HO^\bullet exposure vs. O_3 exposure for ozonation considering the effect Bromide (conditions: $\text{O}_3 = 3 \text{ mg/L}$, pH 7.5, temperature 24°C , Alk.= 2 mM, DOC= 3 mg/L).

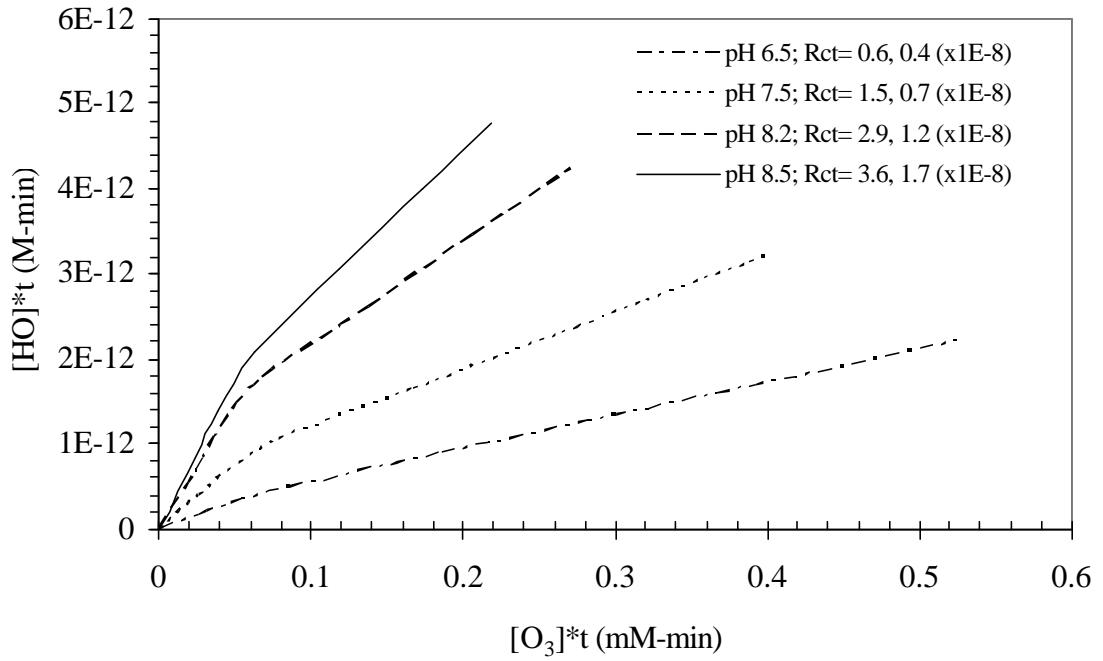


Figure 4.20- HO^\bullet exposure vs. O_3 exposure for ozonation considering the effect pH (conditions: $O_3 = 3$ mg/L, $Br^- = 170$ μ g/L, temperature 24 °C, Alk.= 2 mM, DOC= 3 mg/L).

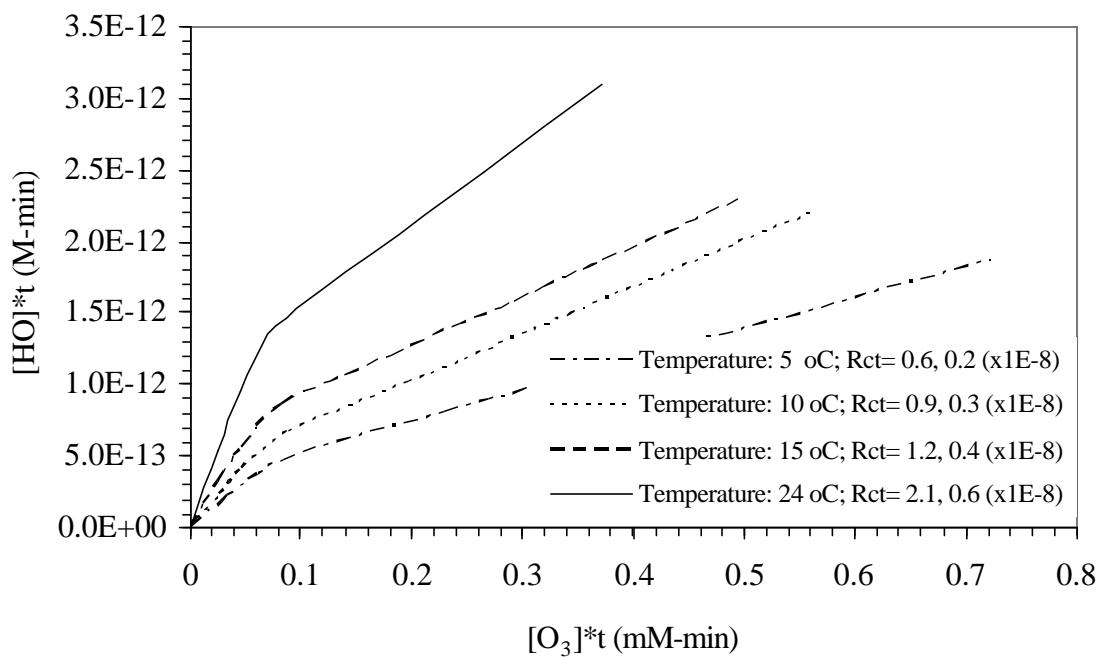


Figure 4.21- HO \cdot exposure vs. O₃ exposure for ozonation considering the effect temperature (conditions: O₃= 3 mg/L, Br⁻=170 µg/L, pH 7.5, Alk.= 2 mM, DOC= 3 mg/L)

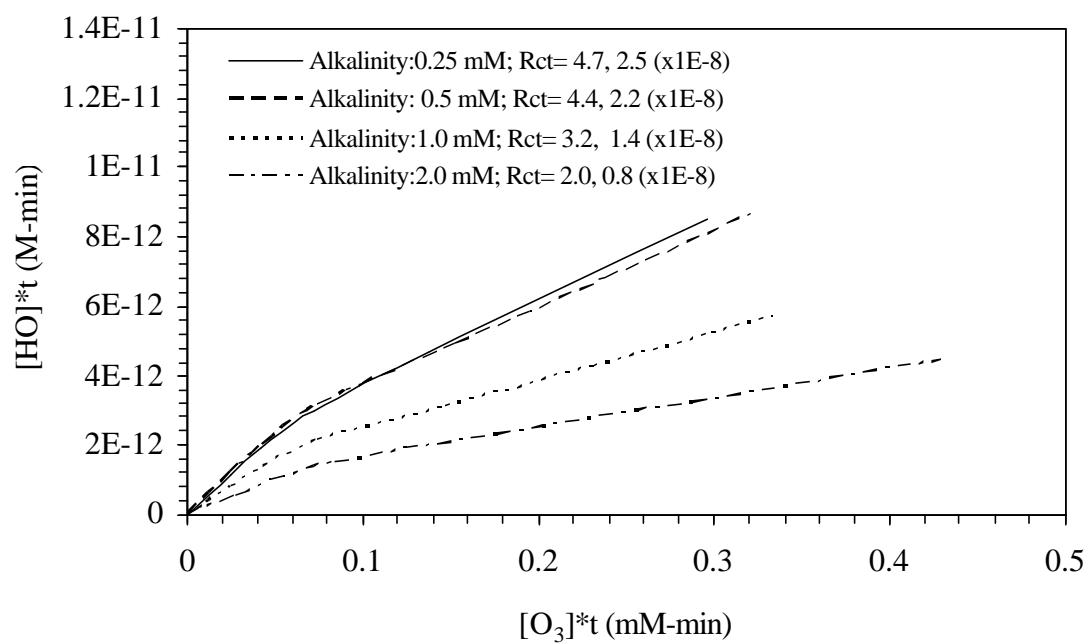


Figure 4.22- HO^{\cdot} exposure vs. O_3 exposure for ozonation considering the effect (bi)carbonate alkalinity
 (conditions: $O_3 = 3$ mg/L, $Br^- = 170$ μ g/L, pH 7.5, temperature= 24 °C, DOC= 3 mg/L)

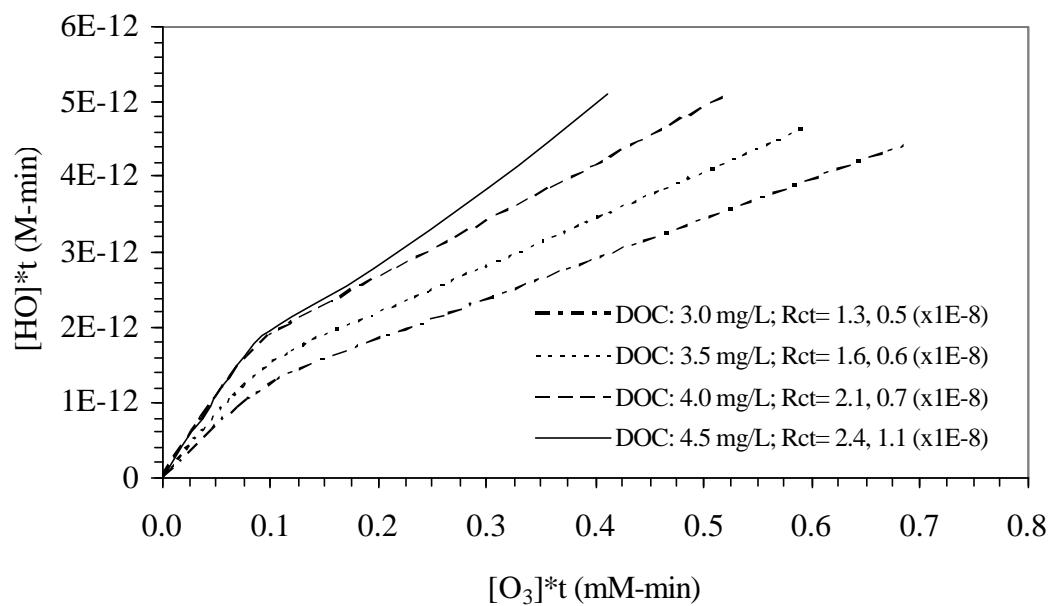


Figure 4.23- HO^\bullet exposure vs. O_3^\bullet exposure for ozonation considering the effect DOC (conditions: $O_3=4.5$ mg/L, $Br^- = 170 \mu g/L$, pH 7.5, temperature= 24 °C, Alk.= 2 mM)

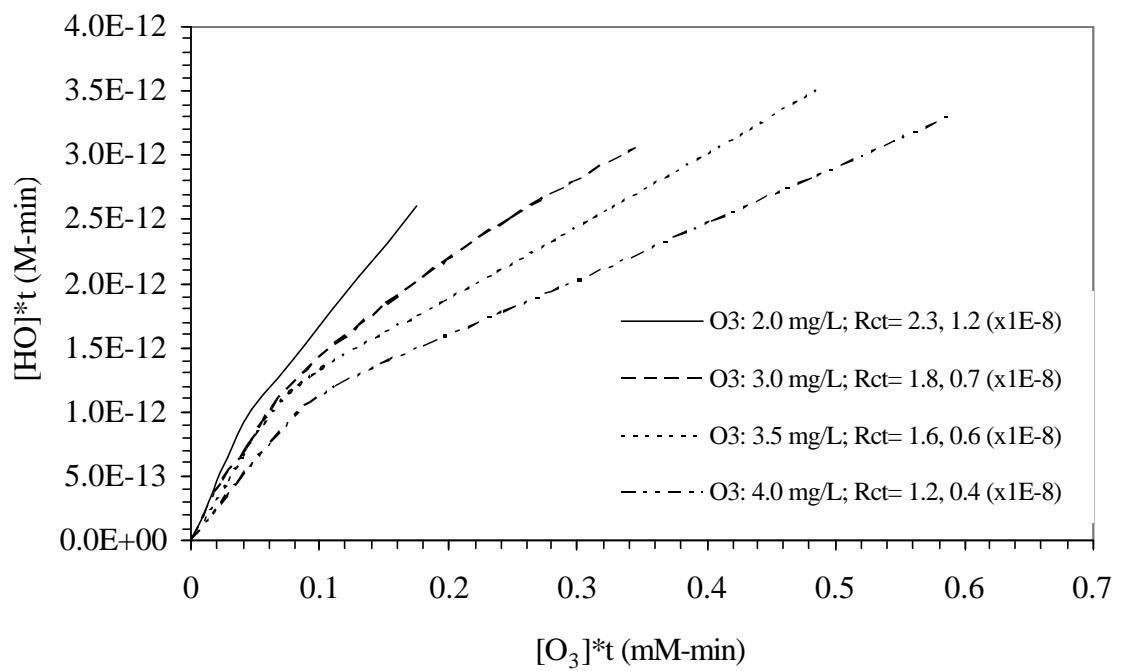


Figure 4.24- HO^{\bullet} exposure vs. O_3 exposure for ozonation considering the effect O_3 dose (conditions: $Br^- = 170 \mu\text{g/L}$, pH 7.5, temperature= 24°C , Alk.= 2 mM, DOC= 3 mg/L)

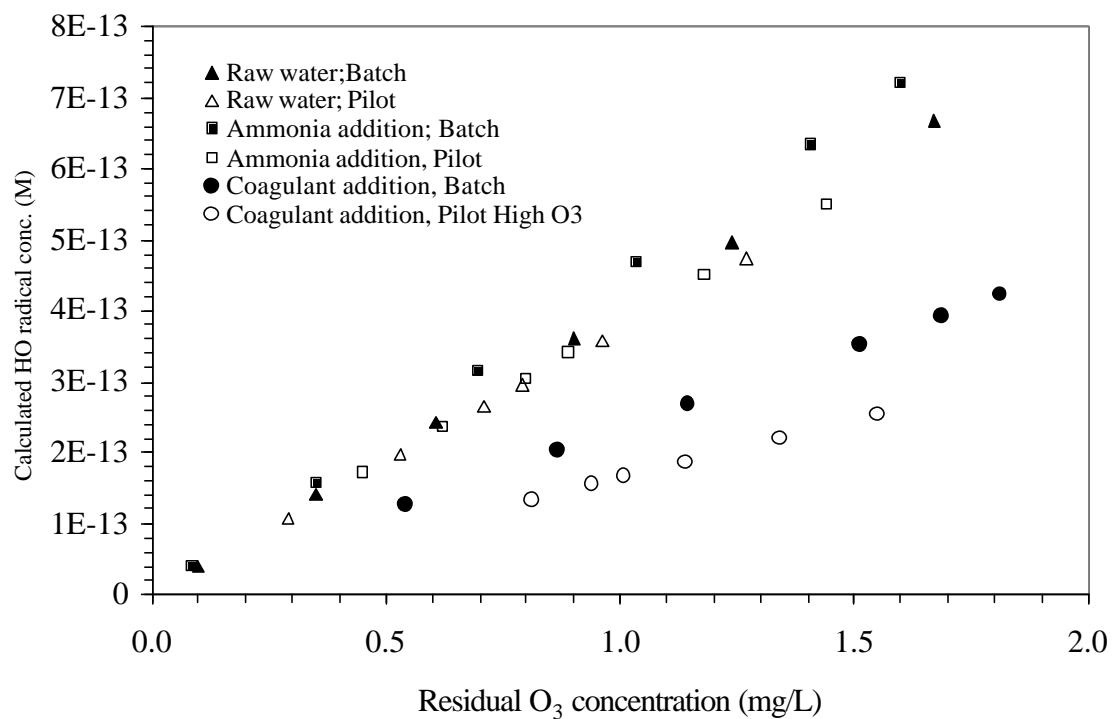


Figure 4.25- Calculated HO[•] concentrations versus O₃ residuals for waters used for pilot-scale and batch ozonation experiments

13. CHAPTER 5

14. EFFECT OF OZONE AND HYDROXYL RADICALS ON BROMATE FORMATION DURING OZONATION

14.1. 5.1 INTRODUCTION

Ozone was first recognized as an effective water disinfectant in 1886 (Vosmaer, 1916). The perception of ozonation as a “clean” oxidation process with fewer harmful disinfection byproducts (DBPs) than chlorination led to a rapid interest by American municipalities in the past two decades (Rice, 1997). More importantly, the inability of chlorine to effectively control waterborne pathogens such as protozoan parasite *Cryptosporidium parvum* (*C. parvum*), an important etiologic agent of waterborne disease outbreak, and the ability to control micropollutants (pesticides, herbicides, endocrine disruptors, and pharmaceuticals), taste and odor compounds (MIB and Geosmin) and reduced inorganics (iron, arsenite, and manganese) has increased the attractiveness of ozone for use as a multiple benefit oxidant/disinfectant (Langlais, et al, 1991, Han et al., 1998 and Staehelin and Hoigne, 1982). However, organic and inorganic DBPs may be formed during ozonation. Among these DBPs bromate (BrO_3^-) is of major concern due to its recognized carcinogenicity. This chapter investigates the effects of water quality and treatment variables on bromate formation during ozonation of waters containing bromide.

Bromate can be formed during oxidation in waters containing the bromide ion (Haag and Hoigne, 1983; Siddiqui and Amy, 1993). In a study of 101 US drinking water sources, including lakes, river, and ground waters, Amy et al., (1994) found a national average bromide level of between 80 and 100 $\mu\text{g/L}$. Despite such low levels of bromide

present in source waters, bromide can be oxidized by ozone and its decomposition by-product, hydroxyl radicals (HO^\bullet) to form bromate. Bromate is strictly regulated due to its suspected human carcinogenic toxicity. Investigation of drinking toxicological studies showed that water spiked with potassium bromate caused kidney tumors in the kidney, thyroid, and mesothelium of rats (Kurokawa et al., 1982). The International Agency for Research on Cancer (IARC) has therefore classified bromate as a Group 2B carcinogen (WHO, 1991). The admissible concentration of bromate in drinking water was estimated using a linearized multistage model assuming a daily consumption of 2 liters of water by a 70-kg adult. Under the estimated lifetime risks of 10^{-4} , 10^{-5} , and 10^{-6} for renal tumors, these assumptions would thus lead to levels of 5, 0.5 and 0.05 μg of bromate per liter of drinking water. However, the present analytical methods for bromate determination have a detection limit of 2-5 $\mu\text{g/L}$. Based on the limitation of detection technology and the priority of safe disinfection, the United State Environmental Protection Agency (USEPA, 1998) regulated the maximum contaminant level (MCL) of bromate in drinking water in the Stage I Disinfectant/DBP Rule (D/DBPR) at 10 $\mu\text{g/L}$, which poses a risk greater than that seen at a value estimated at 10^{-5} . Since either bromate, or its precursor, bromide, removal is difficult (Siddiqui and Amy, 1993); formation of bromate during ozonation should be controlled. Therefore understanding the formation mechanisms and pathways of bromate are keys before addressing bromate control strategies.

During ozonation of bromide-containing waters, two related, yet different, oxidation mechanisms are responsible for bromate formation: pathways involving molecular ozone (O_3) or hydroxyl radicals (HO^\bullet), an ozone decomposition by-product. When ozone is applied, ozone may either react directly with dissolved species or decompose to form secondary oxidants such as HO^\bullet , which may then lead to a series of radical chain reactions accompanied by further ozone consumption. Von Gunten and Hoigne (1994)

introduced a bromate formation model including molecular ozone pathways and HO[•] pathways in water chemistry, shown in Figure 5.1. In general, the relative importance of bromate formation via ozone and HO[•] mechanisms is varied and affected by water quality characteristics and drinking water treatment conditions (Kruithof et al, 1993; Yates and Stenstrom 1993; von Gunten and Hoigne, 1994; Siddiqui et al., 1995; Song et al, 1996 Galey et al., 2000).

In Chapter 4, water quality characteristics such as pH, temperature, (bi)carbonate alkalinity, NOM and bromide level and treatment conditions such as various ozone doses, contact times and/or addition of ammonia (NH₃) or acid have been thoroughly examined as affecting the relative contribution of each pathway as expressed by the value R_{CT}, the ratio of HO[•] exposure (or concentration) versus O₃ exposure (or concentration). In this chapter, a more complete investigation on examining bromate formation during ozonation at different water quality variables and treatment conditions was conducted in order to determine the link between the R_{CT} and formation of bromate. It is hypothesized (*Hypothesis I*) that ‘*bromate formation increases proportionally to the ratio of [HO[•]]/[O₃] during ozonation, affected by different water quality variables (pH, DOC, temperature, ammonia and (bi)carbonate alkalinity) and water treatment conditions (ozone dose, contact time and flow rate)*’. The objective of this study is to characterize two oxidants, molecular ozone and HO[•], in terms of the quantity of R_{CT} (as first introduced by Elovitz and von Gunten, 1999), on the effect of bromate formation during ozonation of natural waters under various water quality and treatment conditions. Furthermore, the intermediate aqueous bromine (HOBr/Br⁻) concentrations formed during ozonation were investigated to better understand the mechanisms of bromate formation and to evaluate control strategies. Methods of bromate control via pH depression and ammonia addition were also investigated. Colorado River water (CRW) was used as the source water because it is a major water supply for six southwestern states in the US.

14.2. 5.2 MATERIALS AND METHODS

Bench-scale batch and continuous flow ozonation experiments were conducted in laboratory and pilot-scale ozonation tests were performed at Union Hills Water

Treatment Plant in Phoenix, Arizona. Details regarding experimental protocol are outlined below:

14.2.1. 5.2.1 Materials:

All chemicals were analytical grade or better and stock solutions for adjusting initial water qualities were prepared with water ($>18\text{m}\Omega$) made from an ultrapure water system (Nanopure InfinityTM). Gaseous ozone was generated by an ORECTM (Model V5-0, Phoenix, AZ) ozone generator from pure oxygen (99.999%). Figure 5.2(a) shows the schematic diagram of stock ozone solution generation for batch experiments and continuous flow ozonation system. The concentrated dissolved O₃ stock solutions were produced by continuously bubbling pure gaseous O₃ through a two-liter glass reactor filled with Nanopure water that was cooled in an ice bath. Gaseous ozone was transported by stainless steel tubing and passed a gas-washing bottle containing 0.5 M phosphate buffer (pH 6) to remove nitric oxidized impurities before dissolving into water. The saturated stock O₃ solution of approximately 40 mg/L ($\epsilon_{258\text{nm}}=3150 \text{ M}^{-1}\text{cm}^{-1}$ @ pH 2) was achieved routinely after an hour.

All experiments were performed using a single source water obtained from the Colorado River conveyed by the Central Arizona Project canal (CRW water). The raw water used for batch experiments was collected at the Scottsdale Water Campus in Scottsdale, Arizona and passed through pre-ashed glass filter papers (GF/F WhatmanTM) to remove particles. Filtered water was stored at 4 °C before use. The pH of all experimental water solutions was adjusted to the desired value by adding prepared stock solutions of sulfuric acid or sodium hydroxide. Experiments involving temperature adjustment were conducted in an incubator equipped with environmental temperature controls. For experiments looking at DOC concentration effects, the desired DOC concentrations were adjusted using additional DOC from a stock solution that was prepared by re-dissolving a CRW DOC isolate previously extracted using a Nano-filtration and XAD-4 membrane technique (Aiken, 1992). Details of the DOC isolation processes are shown in Appendix A. (Bi)carbonate alkalinity was adjusted in sample water solutions by first sparging off all carbonate/bicarbonate contents by adding sulfuric acid to lower pH to approximately 4 and then immediately using pure helium (99.999%) to strip off dissolved carbon dioxide. A stock bicarbonate solution was then used to adjust to the desired (bi)carbonate alkalinity and readjusting pH. Ammonia

chloride was used for adjusting ammonia levels in the water for some experiments. All water samples were spiked with 0.25 µM of para-chlorobenzoic acid (PCBA) before ozonation to measure HO[•] concentration.

14.2.2. 5.2.2 Experimental Procedures

Batch Ozonation Experiments. Batch ozonation experiments were performed by injecting small volumes of the ozone stock to achieve an initial ozone concentration (2-4.5 mg/L) into a 1-L cylinder reactor containing 500 milliliters of prepared waters (Figure 5.2(b)). A Teflon mesh was applied to cover the top of water surface as soon as stock ozone solution was added to prevent the ozone loss by volatilization. Samples were collected over time and immediately analyzed for residual ozone content using the indigo method of Bader and Hoigne (1981). Samples were simultaneously collected to analyze for PCBA, HOBr, bromate and nitrate, after which were immediately bubbled with high flow of pure helium to remove any ozone residual.

Continuous-flow Ozonation Experiments. Gaseous ozone with adjusted flow rates passed first through a 500-mL gas-washing bottle containing a 0.5-M phosphate solution (pH 6). Purified gaseous ozone was then introduced to the bottom of the first 1-L reactor with a diffuser, whereas the countercurrent filtered (0.1 µm AH & DH, WhatmanTM) CRW water with various flow rates flowed into the reactor from the top port (Figure 5.3). Ozone residuals at different sampling ports, which representing different hydraulic retention times, were monitored. When ozone concentrations remained constant over time (reached a steady state condition), water samples were collected at sampling ports 1, 2 and 3 and ozone residuals were stripped off with helium immediately for bromate, nitrate and PCBA analysis. For the separate ammonia addition and pH depression experiments, stock solution of either ammonia chloride or concentrated sulfuric acid was added to the water prior to the experiments. After all the experiments were completed, a blue dye ($\lambda_{\text{max}}= 600 \text{ nm}$) was added into water as a tracer to determine the flow and reactor hydraulics. Detailed results of the tracer tests are shown in Appendix B.

Pilot-Scale Ozonation Experiments. The pilot unit of ozonation operated by Carollo EngineersTM shown in Figure 5.4 consisted of four columns, which is located at the Union Hills Water Treatment Plant in Phoenix, AZ. Gaseous ozone, produced from oxygen with an ORECTTM ozone generator, was bubbled into the base of the first column with countercurrent 4.5 gallons per minutes (gpm) of raw CRW water

delivered from a sedimentation tank flowed into the top of the first column. Chemicals such as PCBA or ammonia chloride were introduced prior to addition into the ozone columns. In addition, ferric chloride and (C_3O_8P) polymer were added to the coagulation/flocculation basins prior to the sedimentation and ozone columns in some experiments. Water samples were collected at several different ports along the columns representing increasing hydraulic retention times for ozone residuals as well as bromate formation and PCBA consumption. For bromate and PCBA samples, the collected samples waters were stripped by helium to remove residual ozone and then stored in 4 °C prior to analysis.

14.2.3. 5.2.3 Analytical Methods

The dissolved NOM-free O_3 concentrations in the stock solution were determined by direct UV absorbance at wavelength 258nm ($\epsilon= 3150 \text{ M}^{-1}\text{cm}^{-1}$) (Langlais et al., 1991). The stock O_3 solution was diluted to an UV absorbance of less than 1.0 cm^{-1} with diluted phosphoric acid to remain in the linear portion based upon Beer's Law. Because NOM interferes at a wavelength of 258 nm, for waters containing NOM, dissolved O_3 residual was measured with a Shimadzu™ UV/Vis spectrophotometer using an indigo colorimetric method (Bader & Hoigne, 1981). Solution pH and temperature were measured using a Bechman™ pH electrode, which was calibrated with standard buffers (J. T. Baker™). DOC concentrations were determined by a Shimadzu™ TOC 5050 Analyzer. Water (bi)carbonate alkalinity was measured by a Hach™ kit colorimetric titrator.

Aqueous bromine (HOBr/OBr^-) was measured using a Hach™ pocket colorimetric spectrophotometer. Bromide, bromate and nitrate were measured using a Dionex™ ion chromatograph. The system included an anion self-regenerating suppressor and conductivity meter and the columns used included a Dionex™ AG9-HC guard column to prevent potentially fouling the AS9-HC analytical column. The analytical method included an eluent of 9.0-mM sodium carbonate, 1.0-mL/min flow rate, and a 500- μL injection loop. Bromate samples were pretreated to remove abundant chloride ion (Cl^-) existing in the CRW water using Dionex™ OnGuard-Ag and -H cartridges (for removing residual Ag) connected in series since in ion chromatograph, the Cl^- peak is adjacent to BrO_3^- peak and high Cl^- concentration results in overlap on BrO_3^- peak.

PCBA was determined using a Waters™ high performance liquid chromatograph (HPLC) fitted with a reverse-phase (RP-18) analytical column and a 500- μ L injection loop using a 55% methanol and 45% 10 mM phosphoric acid mobile phase with a flow rate of 1.0-mL/min. Detection was made using an UV detector set to a wavelength of 234 nm.

14.3. 5.3 RESULTS

Table 5.1 summarizes important water quality parameters of the raw CRW water collected at Scottsdale Water Campus, Scottsdale, AZ on March 12, 2001. Using the ambient CRW water quality as a basis of comparison, a number of bench-scale batch and continuous flow CRW water ozonation experiments were conducted in which each experiment was under a set of adjusted water quality and treatment conditions. The CRW water used for pilot ozonation experiments was not collected from the same date as for bench-scale experiments, important parameters such as ambient bromide level, pH, (bi)carbonate alkalinity and concentration of DOC remained nearly unchanged. In general, the annual CRW water pH is usually greater than 8.0; and concentrations of DOC and (bi)carbonate alkalinity are approximately 3 mg/L and 100 mg/L as CaCO₃, respectively.

14.3.1. 5.3.1 Ozone Demand and Decay

Tables 5.2 and 5.3 are the experimental matrices used for the overall batch and continuous flow ozonation experiments, respectively. Pilot-scale ozonation experiments were based upon the experiment matrix shown in Table 5.4 and conducted at the Union Hills Water Treatment Facility in Phoenix, AZ. In general, ozone decay characteristics vary by varying water quality parameters (e.g., bromide level, pH, temperature, (bi)carbonate alkalinity and DOC concentration) and treatment variables (e.g., O₃ dosage, contact time and addition of acid or ammonia) in batch ozonation experiments. Previous chapters have described a three-staged ozone consumption during batch ozonation experiments regardless of different adjusted water quality conditions and various treatment variables. Figure 5.5 shows an example of ozone decomposition curves and HO• concentrations over time during ozonation at four different initial bromide levels. Increasing initial bromide concentrations result in a small increase of ozone residual demand, but lower HO• concentrations by a factor of 2 to 3. This suggests that bromide species actively scavenge HO•.

Only the slow-stage (e.g., reaction time > 2 minutes) ozone decay was able to be observed in the bench-scale continuous flow and pilot-scale ozonation experiments (data not shown). In addition, ozone demand, determined by varying ozone dosages, represents the maximum ozone dose that does not result in an ozone residual. Magnitude of ozone demand is an important parameter and can usually represent the quality of water. More importantly, knowing the ozone decay and demand is key in determining initial ozone dose in order to guarantee sufficient ozone residual (CT concept) for water disinfection. Figure 5.6 shows the ozone demand curve at five ozone dosages for CRW raw water. Ozone demand for raw CAP water is equivalent to the values of the intersection of the curve at X-axis, which is 0.87 mg/L.

14.3.2. 5.3.2 Bromate Formation and Control

The rate and extent of bromate formation are different in each experiment and, in general, are governed by water quality variables and treatment conditions already mentioned above. Figure 5.7 shows an example of kinetic bromate formation in batch ozonation experiments varying bromide concentrations. In comparison with O_3 decomposition, kinetics of bromate formation is somewhat inversely symmetric to its O_3 decay curve. Higher rates of bromate formation occurred during the fast reaction stage (e.g., reaction time < 2 minutes) and is followed by gradually decrease of rate over time at the slower reacting stage, due in part to both decreasing Br^- concentration and O_3 residual over time. Figure 5.7 also shows the change of intermediate aqueous bromine (e.g., sum of $HOBr$ and OBr^-) concentration over time during ozonation. It is observed that the bromine concentration initially accumulates up to a molar concentration of 40% of the initial bromide (molar) concentration during the first 10 minutes, followed by gradually decrease afterwards.

In both bench- and pilot-scale continuous ozonation systems, O_3 was only introduced in the first reactor (column). Because profiles of ozone decomposition and

bromate formation in the first reactor were not determined due to experimental setup, measured results are consistent with the slow-stage of ozonation (e.g., HRT> 2 minutes). It is observed that trends of ozone decomposition and kinetic bromate formation in bench- and pilot-scale continuous flow ozonation are similar to bench-scale batch ozonation. Figure 5.8 demonstrates examples of change of ozone residuals and bromate formation over time in bench- and pilot-scale ozonation.

Bromate can be formed during ozonation with most water quality parameters affecting bromate formation. It would not be surprising that in ozonated waters containing significant level of bromide, the MCL could easily be exceeded. Therefore, developing proper strategies to minimize bromate formation while still maintain the disinfection capacity of ozone have become imperative. Based upon the accumulated knowledge on understanding the effects of water chemistry on bromate formation during ozonation, a number of methods to resolve unwanted bromate formation have been proposed, including 1) reduction of initial water bromide level, 2) scavenging HO radicals, 3) lowering intermediate hypobromite ions (OBr^-) during ozonation, or 4) removing bromate after ozonation. In drinking water treatment, however, the reduction of intermediate OBr^- concentration by decreasing water pH and/or addition of ammonia are probably the most applicable options in controlling bromate formation (Pinkernell and von Gunten, 2001). In this study several ozonation experiments at different ammonia concentrations and pH conditions were conducted to investigate their impact on reducing bromate formation.

Sulfuric acid addition for depressing pH effectively reduces bromate formation, although usually leads to higher ozone residuals. Figure 5.9 shows that at

comparable treatment conditions (O_3 : 3 mg/L; temperature: 24 °C), the kinetics of bromate formation became slower when pH was decreased from an ambient value of 8.2 to 7.5 and 6.5. Compared to ambient water pH, a reduction of up to 30% and 80% of bromate can be observed at 20 minutes when water pH was lowered to 7.5 and 6.5, respectively. This could be explained by the fact that pH depression inhibits both direct and indirect pathways of bromate formation by decreasing hydroxide ion (HO^-) and HO^\bullet concentrations as well as shifting the intermediate OBr^- to its conjugate acid form, e.g., HOBr, which does not tend to oxidize into BrO_3^- ion. At pH 6.5, bromate was reduced to control the concentration of bromate below 10 µg/L after 20 minutes. However, bromate levels at an equivalent CT of 1.5 mg/L-min (~ one log Cryptosporidium inactivation) was 6, 13, and 18 at pH 6.5, 7.5 and 8.5, respectively.

Another alternative for reducing bromate formation is by reducing the intermediate OBr^- concentration during ozonation by (adding) ammonia. Figure 5.10 shows bromate formation over time in batch ozonation experiments with various dosages of ammonia addition in terms of molar ratio of NH_4^+ / Br^- (0-60). The results show that significant bromate removal efficiency was achieved with the addition of only 0.03 mg-N/L of ammonia (NH_4^+ / Br^- molar ratio=1). Increasing ammonia doses lead to further bromate reduction efficiency. Up to 65% of bromate was reduced when 0.9 mg-N/L of ammonia (NH_4^+ / Br^- molar ratio=30) was added compared to water without any ammonia addition. However, the reduction of bromate by adding ammonia is not infinite and is limited by intermediate HOBr. Even though HOBr reacts rapidly with ammonia, some bromate will still form via dissociation (OBr^-) and subsequent oxidation by the HO^\bullet pathways. However, close examination of the

bromate kinetics shown in Figure 5.10 indicated efficient bromate control appeared after 2 minutes. During the first 2 minutes of ozonation, the highest HO[•] concentrations occur and, meanwhile, very low limited intermediate HOBr formed. Thus, ammonia did not perform effectively bromate reduction by scavenging HOBr. Since the consumption rate of HOBr ($-d [HOBr]/dt$) by ammonia is overwhelmed predominant compared with ozone and HO[•], it is reasonable to assume that the majority of intermediate HOBr is consumed by ammonia when the stoichiometric NH₄⁺ versus Br⁻ is in excess. Therefore, it can be inferred that at 20 minutes of ozonation, approximately 35% of bromate was formed by HO[•] pathways.

Similar trends on bromate reduction by addition of acid and ammonia were observed in bench- and pilot-scale continuous flow ozonation experiments. Figure 5.11 demonstrates bromate reduction by the addition of ammonia and sulfuric acid during bench-scale continuous flow ozonation. Ammonia addition and pH depression effectively performs bromate formation control. It was observed that when treatment conditions are held unchanged (e.g., same ozone dose and water flow rate applied), approximately 11%, 37%, and 65% of the bromate was reduced by the addition of ammonia on the basis of NH₄⁺/Br⁻ molar ratio of 1, 3, 10, respectively, while almost 35% of bromate was reduced when ambient water pH of 8.2 was lowered to pH 7.

When different water flows were applied to determine how the factor of hydraulic retention time affects bromate formation, it was observed that bromate formation is proportional to the HRT. That is, the higher the HRT, which represents longer reaction time, increases in bromate production were observed. Figure 5.12

shows a good linear relationship between bromate formation and HRT quantified below as:

$$\text{Bromate } (\mu\text{g/L}) = 2.6 \times \{\text{HRT}\} - 3.0$$

5-1

It can be concluded that bromate formation is directly proportional to water hydraulics expressed in terms of HRT, under a constant applied ozone dose.

14.4. 5.4 DISCUSSION

14.4.1. 5.4.1 Parameters Affecting Bromate Formation

Water chemistry influences bromate formation. Bench-scale studies show that bromate formation during ozonation in waters containing bromide is a function of the following water quality parameters:

- Ozone dose
- Initial bromide level
- pH
- Temperature
- NOM
- (Bi)carbonate alkalinity
- Ammonia

It is observed that the water quality parameters bromide level, temperature, pH and (bi)carbonate alkalinity are positively correlated with bromate formation while DOC and ammonia have an inverse impact on bromate formation. In addition, when considering treatment conditions such as O_3 dosage and O_3 contact time, as expected, higher amount of applied O_3 results in faster bromate formation while the bromate concentration continuously increases over time until Br^- ion and/or O_3 residual are depleted.

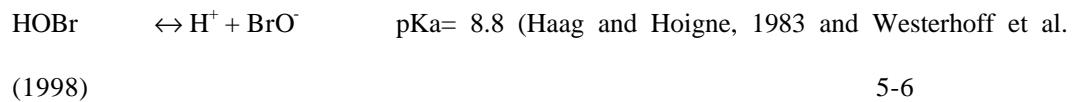
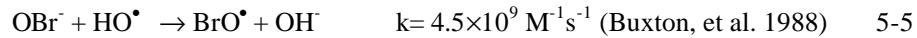
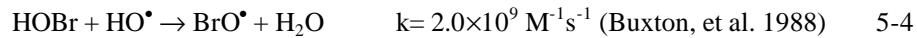
All these factors may influence rates of ozone decomposition and/or HO[•] production thus affecting the overall kinetics of bromate formation and relative amount of formed bromate. In addition, they can also directly and indirectly affect bromate formation by reacting with intermediate bromine species (e.g., Br⁻, HOBr/BrO⁻, Br[•] and BrO[•], etc.). Details of how each of these parameters effects bromate formation are discussed below:

Effect of ozone dose. Applying higher initial O₃ dosage leads to more bromate formation due to increasing reactants' driving force of both ozone and HO[•] to oxidize bromide. Ozone is a strong oxidant capable of reacting with a variety of constituents in water. When these organic and inorganic species exist in water, they can consume O₃ and compete with bromide by reacting with molecular O₃ and HO[•]; and thus increasing overall ozone demand. This is especially true when waters containing NOM have high aromatic content (Song, et al., 1996). When a higher O₃ dose is applied, higher O₃ residual still remains in the water after being rapidly consumed by other organic and inorganic species, therefore leading to higher bromide oxidation capabilities.

Effect of Bromide concentration. Under the same treatment conditions, increasing the initial bromide concentration will result in a proportional increase of bromate concentration which agrees with Amy et al's (1993) observation. Based upon reaction kinetics, the bromide ion is a primary reactant and, as expected, higher initial bromide concentrations produce a higher chemical gradient, which drives the reactions toward the product's direction (e.g. bromate formation). Since both molecular O₃ and HO[•] react with Br⁻ and partially contribute to bromate formation, higher Br⁻ concentration leads to higher HO[•] scavenging thus stabilizing ozone decomposition by inhabiting a series of free radicals chain reactions. This process of HO[•] scavenging by Br⁻ results in the formation of more bromate while enhancing Br⁻ oxidation with higher remaining O₃ residual.

Effect of pH. Rate of ozone decomposition as well as bromate formation is a function of pH; and will increases with increasing pH. This agrees with previous studies conducted by von Gunten and Hoigne (1993), Westerhoff, et al. (1993) and Song, et al. (1996). Several factors that lead to bromate formation are affected strongly by water pH. First, based upon the ozone decomposition mechanism proposed by Langlais et al. (1991), higher OH⁻ ion concentration will occur at higher pH leading to the formation of more HO[•], which will result in the formation of more bromate. Second, comparing rate reactions of

HOBr/OBr^- with molecular O_3 and HO^\bullet shown below (Eqn. 5-2 to Eqn. 5-6), increasing pH shifts the HOBr to OBr^- , which is more reactive to both molecular O_3 and HO^\bullet ; thus forming more bromate.



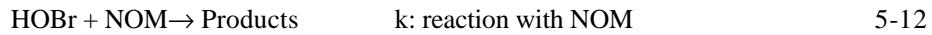
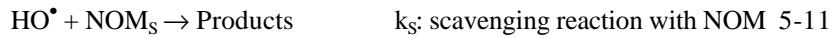
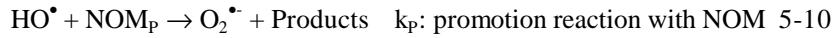
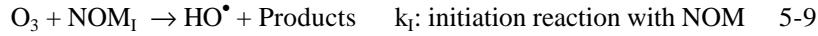
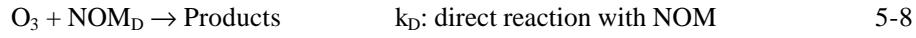
Third, increasing pH will increasingly deprotonate NOM and change the protonation of inorganic carbonate species, which could increase the rate of HO^\bullet generation, and therefore, increasing bromate formation. This trend will be detailed further in this discussion.

Effect of Temperature. Rate of bromate formation will increase as increasing water temperature during ozonation. However, literature reports of temperature effects on bromate formation are limited. From the Arrhenius' empirical rate law, the rate constant of k is a function of temperature based upon the following equation:

$$k = f(e^{-E/RT}) \quad 5-7$$

where k = rate constant; T = absolute temperature; E = activation energy; R = universal gas constant. With an activation energy of 92 kJ/mol for ozone decomposition, and 37 and 60 kJ/mole for the reactions of ozone with Br^- and OBr^- , respectively, reaction rates at 20°C for ozone decomposition, the reaction of ozone with Br^- and with OBr^- will be 4.0, 1.7, and 2.4 times higher than at 10 °C, respectively. Although ozone decomposes more rapidly with increasing temperature resulting in less remaining ozone, bromate formation appears to be more dependent upon the proportionate effects of kinetic and thermodynamics factors. Siddiqui (1992) reported a slight increase in bromate formation resulting in only a 2% to 16% increase of bromate from baseline condition. Our study, however, shows that temperature is an important parameter in terms of bromate formation, which agrees with study by Driedger et al. (2001). It is observed that rate of bromate formation is proportional to change of temperature. When water temperature increased from 4°C to 15 °C and to 24 °C, bromate formation increased by approximately 25% and 50%, respectively, when remaining other parameters unchanged.

Effect of NOM concentration. NOM can react with ozone, HO[•] and intermediate HOBr in a series of chain reactions during ozonation. The followings are simplified reactions of NOM with ozone, HO[•], and HOBr:

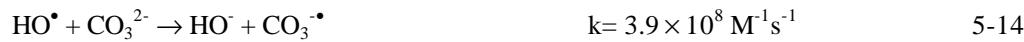


In general, the concentration of NOM has an inverse impact on bromate formation during ozonation in the presence of bromide ions. The chemical composition of NOM also appears to influence this as well. Equation 5-8 to 5-12 depicts the effect of NOM on the chemistry of ozonation in several ways and thus results in reduction of bromate formation. Equation 5-8 shows that a rapid direct reaction of O₃ with some active constituents of NOM can effectively reduce the opportunity of molecular ozone to oxidize bromide species. These constituents of NOM may act as initiators, promoters, and intimidators of the HO[•] chain reactions as shown in Equations 5-9 through 5-11, consuming both molecular ozone and HO[•]. Similarly, HO[•] and superoxide (O₂^{•-}) ions formed from a series of radical chain reactions will result in more consumption of molecular ozone. The formed intermediate HO[•], however, may also be responsible for some bromate production. Results in our batch experiments examining the effects of DOC at different incremental DOC concentrations show that the overall HO[•] exposure slightly increases at higher DOC concentrations while O₃ exposure gradually decreases (Figure 5.13). This might be due to specific NOM characteristics (e.g., those of humic materials) reacting with HO[•] to produce chain carriers of O₃ decomposition and increasing the HO[•] formation rate. DOC levels and composition will both affect both ozone and HO[•] concentrations required for bromate formation.

NOM can also react with hypobromous acid to form bromo-organic species, thus serving as a sink for bromide. Based upon available concentrations and rate constants of O₃, HO[•], DOC and intermediate aqueous bromine, the fraction of aqueous bromine consumption by DOC can be estimated. Up to 20% of intermediate aqueous bromine was lost to bromo-organics formed from ambient water NOM. Therefore, it

may conclude that the reaction of NOM with aqueous bromine could play an important role in bromate reduction.

Effect of (Bi)carbonate Alkalinity. Water (bi)carbonate alkalinity acts an important role in ozone decomposition and bromate formation. According to the definition of alkalinity (Carbonate alkalinity= $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$), the effect of alkalinity can be related to the effects of total inorganic carbon (TIC) at a constant pH value. This is due to the fact that typical pH values of natural waters are within the range of between 6 and 9, and thus the majority of total alkalinity is from the two carbonated species. During ozonation, both bicarbonate and carbonate ions are capable of scavenging HO[•] and form secondary inorganic carbon radicals (CO₃^{•-}) (Buxton et al., 1988). Therefore, carbonate species can directly effect ozone decomposition, which in turn will promote the direct oxidation pathway for bromate formation based on the following reactions:



In addition to enhance ozone oxidation on bromide species, active carbonate radicals, on the other hand, can oxidize both OBr⁻ and BrO₂⁻ and form bromate precursors (e.g., BrO[•] and BrO₂[•]), which results in forming more bromate via disproportionation. Our results show that increasing the (bi)carbonate alkalinity of 10-fold (from 20 to 200 mg/L as CaCO₃) resulting in a 3-fold of bromate formation, which agrees to a conclusion stated by Song et al (1994) that a significant increase in bromate with addition of total inorganic carbon. In addition, because the reactivity of HO[•] with carbonate ions is 45 times higher than with bicarbonate, increasing the water pH will shift the carbonate species toward carbonate and, therefore, it may imply that at higher water pH will leads to forming more coronate ions and hypobromite ions and thus enhancing the effect of (bi)carbonate alkalinity on bromate formation.

Effect of ammonia addition. Ammonia rapidly reacts with intermediate hypobromous acid formed from oxidation of bromide and then to form bromamines, which will inhibit the oxidation pathway of bromide to bromate (von Gunten and Hoigne, 1994). The effect of ammonia on bromate formation have

been investigated by a number of researchers (Haag et al., 1984; Hoigne t al, 1985; Amy et al., Hofmann, 2000) and concluded that increasing ammonia concentrations resulted in a decrease in bromate formation. The following three reactions show that ammonia reaction with HOBr and ozone are a function of pH and can play a role of bromide catalyst by regenerating bromide through the $\text{Br}^- \rightarrow \text{HOBr} \rightarrow \text{NH}_2\text{Br} \rightarrow \text{Br}^-$ cycle, which results in a lag period before bromate formation occurs (Haag et al., 1984).



Results from batch and continuous flow ozonation experiments show that addition of ammonia effectively reduces the bromate formation even at low ammonia concentrations (<0.03mg-N/L). However, although reactions of O_3 with ammonia ($k = 20 \text{ M}^{-1}\text{s}^{-1}$) and bromamine ($k \approx 40 \text{ M}^{-1}\text{s}^{-1}$) species are slow, the O_3 decomposition starts being affected when a very high dose of ammonia is added. Figure 5.14 shows that when the molar ratio of $\text{NH}_4^+/\text{Br}^-$ is greater than 15 ($\text{NH}_3 \approx 0.5 \text{ mg-N/L}$), the rate of O_3 decay started accelerating and significantly increased by >10%. On the other hand, although ammonia can be a HO^\bullet scavenger ($k = 8.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$), the reaction is not as fast as with NOM and other chemical constituents (Table 5.5). In addition, Br^\bullet and BrO^\bullet oxidized from bromide ions by HO^\bullet most likely do not react with ammonia. Thus, the effect of ammonia on HO^\bullet reaction is probably not important. It can be concluded that additional bromate reduction is probably attributed to consumption of ozone by excess mount of ammonia.

It should be noticed that due to HO^\bullet indirect pathways of forming bromate, ammonia (addition) can not totally reduce bromate formation even at very high level. Our results show that at pH 7.5, approximately 35% of bromate still remained when 1.8 mg-N/L of ammonia was added compared to zero ammonia addition. Therefore, when bromide concentration is high, addition of ammonia for bromate

control probably still cannot reduce bromate down to MCL without any further bromate reduction treatment.

14.4.2. 5.4.2 Relationship between Bromate Formation and Ozone Exposure

Ozone exposure has been applied to measure the power of pathogenic microorganisms' inactivation in logarithm scale and typically expresses as a CT value in which C represents the concentration of O_3 residual and T represents the batch contact time (Hoff, 1987). During drinking water ozonation process, CT-calculations are performed with a conservative approach due to the integral CT-value is not easily accessible in non-ideally behaving reactors. Typical CT values are determined by the residual O_3 concentration at the outlet of the reactor multiplies by the contact time T_{10} , corresponding to the time required for 10% of an applied tracer to travel through the reactor. However, this approach could lead to an underestimation of the integral CT in the reactor, and results in excessive amount of by-product formation (von Gunten, et al., 2001).

In this study integrated ozone exposure (IOE), defined as integration of the O_3 decay curve over time, was applied to determine its relationship with BrO_3^- formation during ozonation process. Figure 5.15 through Figure 5.20 show bromate formation versus IOE under different water quality variables and extents. R_{CT} values were presented in Chapter 4. Bromate formation potential can be determined based on the goal of ozone exposure. It is observed that similar to curves of bromate formation versus contact time; maximum bromate formation rate occurs initially and followed gradually accumulation of bromate as increasing IOE during batch ozonation. These figures show that different water quality variables influence IOE and thus affect bromate formation extent. In other

words, when applying the same IOE exposure, a positive effect on increasing bromate formation as increasing levels of water quality parameters such as bromide level, temperature, pH, and (bi)carbonate alkalinity whereas concentration of DOC shows moderate impact on bromate formation. In addition, ammonia performs a strong inverse impact on bromate formation even at very small change in concentration while IOE exposures remain unchanged.

Daw, et al (2001) proposed that a linear relationship between BrO_3^- and IOE in batch ozonation under non-Br⁻ limiting conditions. However, in practical ozonation of bromide containing waters, bromide concentration is low (typically in parts per billion ranges) and the concentration decreases over time. Equation 5-21 expresses BrO_3^- concentration as a function of IOE shown below:

$$[\text{BrO}_3^-] = K \times [\text{IOE}] + Y \quad 5-21$$

where, K represents BrO_3^- formation slope coefficient in $\mu\text{g}/\text{mg}\cdot\text{min}$ and, as expected, is affected by water quality parameters at various levels and treatment conditions and Y represent bromate concentration at zero IOE. Table 5.6 shows a linear relationship between BrO_3^- formation and IOE in batch ozonation experiments at slow-stage ($t > 2$ min.). However, rapid BrO_3^- formation in the fast-stage (< 2 min.) shows a non-linear relationship between bromate formation and IOE compared against the overall process. Similar to the observation by Driedger et al., (2001) that indirectly oxidation pathways of bromide by HO[•] contribute the major bromate formation at this stage. Further more, it is observed that based on the values of Y, concentrations of HO[•] are affected by water quality parameters and their extents.

14.4.3. 5.4.3 Relationship between Bromate Formation and R_{CT}

Bromate formation chemistry in ozonated waters containing bromide is very complex that involve characteristics of water quality such as bromide, pH, temperature, (bi)carbonate alkalinity, ammonia, and

NOM to react with ozone in which resulting a series of bromide oxidation in ionic and radical forms (Figure 5.1). Due to the incentive of knowing ozone is a powerful disinfectant/oxidant and bromate formed during ozonated waters containing bromide is a troublesome possible carcinogenic disinfection by-product and thus needs to be removed and/or reduced, a number of researches have been conducted worldwide investigating mechanisms and pathways of bromate formation, model prediction on potential bromate formation, microorganisms inactivation, and bromate formation control, etc. However, lack of accurate empirical HO[•] data during ozonation process results in either neglecting the role of HO[•] on disinfection and/or DBP formation or incapable to use mechanical models to accurately predict DBP formation. Recently, a “R_{CT}” approach proposed by Elovitz and von Gunten (1999 & 2000) that by just simply adding trace amount of HO radical probe, PCBA, HO concentrations are, therefore, able to be monitored throughout the ozonation process.

Changes of O₃ and HO[•] concentrations by water quality and water treatment parameters listed above are quantifiable. Previous study by Elovitz and von Gunten (1999 & 2000) and our group showed that the R_{CT}, expressed as a ratio of $\int[\text{HO}^*]/[\text{O}_3]$ (or $[\text{HO}^*]/[\text{O}_3]$), remains unchanged through ozonation process and thus HO[•] concentration can be indirectly measured by calculating the slope coefficient of change of logarithmic PCBA versus ozone exposure. In previous chapters, we concluded that water quality variables and treatment conditions affect values of R_{CT}, and, in general, perform a linear relationship with levels of each parameter. In addition, we also found that extent of bromate formation affected by R_{CT} has a linear relationship with R_{CT} values. Table 5.7 shows that values of R_{CT} and rates of bromate formation are linearly changed by levels of each parameter while holding other parameters constant. Therefore, the hypothesis that changes of bromate formation is linear to the ratio of $[\text{HO}^*]/[\text{O}_3]$ during ozonation, and is affected by different water quality variables (pH, DOC, temperature, ammonia and (bi)carbonate alkalinity) and water treatment conditions (ozone dose, contact time and flow rate). However, an exception is that ammonia does not seem to significantly change R_{CT} value, although increasing amount of ammonia resulting in significantly change of bromate reduction. Ammonia, therefore, affects non-HO[•] mediated BrO₃⁻ form reactions, specifically molecular oxidation of OBr⁻.

14.5. 5.5 CONCLUSIONS

Kinetics of O_3 decomposition and HO^\bullet production as well as bromate formation during ozonation process are governed by water quality characteristics and treatment conditions. Among those parameters, ozone dose, initial bromide concentration, pH, temperature, and (bi)carbonate alkalinity act positive effect on bromate formation, whereas DOC concentration and ammonia perform inverse effect on bromate formation. Previously, Chapter 4 discussed that R_{CT} , an expression of ratio of HO^\bullet exposure (or concentration) to O_3 exposure (or concentration) during ozonation process remains unchanged for a given water under fixed conditions. In addition, two R_{CT} values (fast and slow) observed in ozonation process are influenced by water quality characteristics and treatment conditions as well. Table 5.8 summarizes general impacts on R_{CT} and bromate formation among the above parameters.

In general, R_{CT} values increase proportionally with increasing levels of pH, temperature and DOC and increasing rate of bromate formation except DOC, which acts as inverse impact on bromate formation. On the other hand, R_{CT} values decrease proportionally with increasing bromide and inorganic carbon concentrations, which resulting in increase of bromate formation. Ammonia acts as treatment that efficiently reduces bromate formation. Increasing ammonia's dose enhances reduction rate of bromate formation while still maintaining R_{CT} unchanged. In addition, treatment variables such as ozone dose and reaction time act proportionally impact on rate of bromate formation. Appendix C shows linear regression plots of the values of R_{CT} versus the water quality parameters and treatment variables.

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Table 5.1 - Summary of CRW water quality used for bench-scale ozonation experiments.

Parameters	Values
pH	8.2
Temperature	24 °C
Br ⁻	70 µg/L
Cl ⁻	75 mg/L
Alkalinity	105 mg/L as CaCO ₃
DOC	3 mg/L
UVA _{@254nm}	0.031 cm ⁻¹
Ammonia	< 0.01 mg-N/L

Table 5.2- Experimental matrix for batch ozonation experiments with CRW water.

Parameter	Condition
Ozone Dose	2, 3*, 3.5, 4 mg/L
Temperature	4, 10, 15, 24* °C
pH	6.5, 7.5*, 8.2 (ambient), 8.5
DOC	3*, 3.5, 4, 4.5 mg/L
Alkalinity	10, 30, 50, 105*
Bromide	70, 170*, 320, 450 µg/L
Ammonia/bromide	0*, 0.25, 0.5, 1, 3, 5, 15, 30, 60

*: Baseline conditions

Table 5.3- Experimental matrix for bench-scale continuous flow ozonation experiments with CRW water.

Parameter	Condition
Hydraulic retention time	150, 200*, 250, 400, 500 mL/min
pH	6.5, 7.5, 8.2* (ambient)
Ammonia/bromide	0*, 1, 3, 10

*: Baseline conditions

Table 5.4- Experimental matrix for pilot-scale continuous flow ozonation experiments with CRW water.

Test No.	O ₃ dose (%)	Conditions
1	1.90	Ambient water: pH 8.2, Temperature: 24 °C
2	1.90	Ammonia addition (NH_4^+ /Br ⁻ : 3-[NH ₃ -N]: 0.3 mg/L)
3	1.14	Coagulant addition (16 mg/L FeCl ₃ & 0.35 mg/L C ₃ O ₈ P polymer)
4	0.65	Coagulant addition (16 mg/L FeCl ₃ & 0.35 mg/L C ₃ O ₈ P polymer)

Table 5.5- Rate constants of chemical constituents with HO[•].

Compound (i)	K _{HO[•],i} (M ⁻¹ s ⁻¹)	Reference
Br ⁻	5.0×10 ⁹	Buxton, 1968
BrO ⁻	4.2×10 ⁹	Buxton, 1968
Cl ⁻	4.2×10 ⁹	Buxton, 1968
CO ₃ ²⁻	4.0×10 ⁸	Buxton, 1968
NH ₃	1.7×10 ⁷	Meyerstein, 1972
NOM	4.8×10 ⁸	Kim et al., 2000
PCBA	5.0×10 ⁹	Haag, and Hoigne, 1981

Table 5.6- Bromate formation slope coefficient (K value) in batch ozonation experiments (baseline conditions: O₃: 3 mg/L, Bromide: 170 µg/L; Temperature: 24 °C; pH 7.5; Alkalinity: 100 mg/L as CaCO₃; DOC: 3 mg/L).

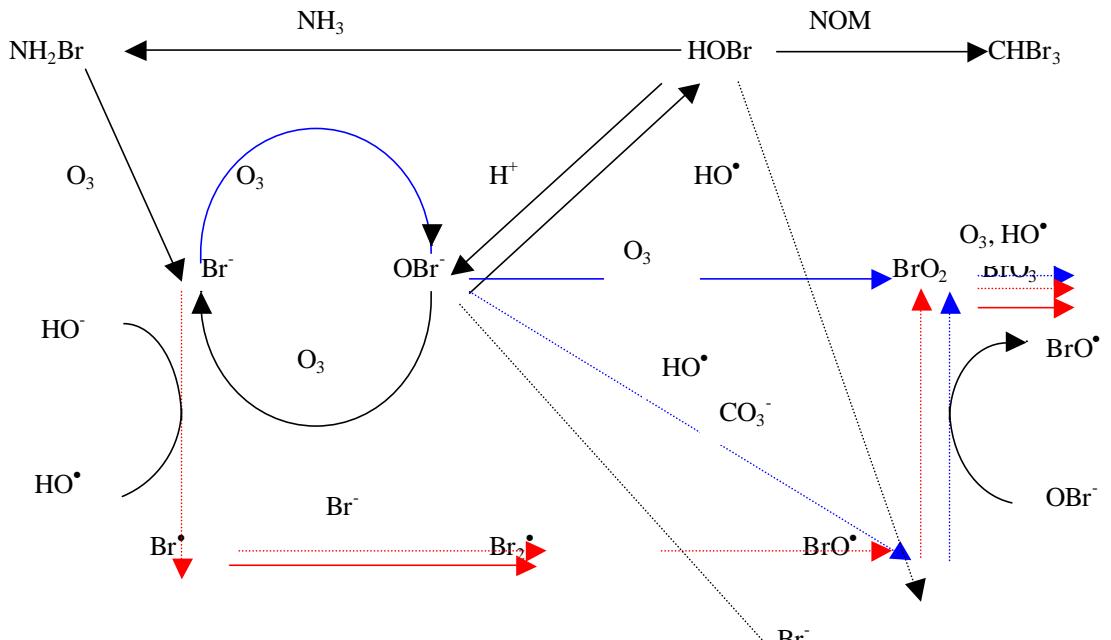
Parameters	Values	Units	K (µg/mg-min)	R ²	Y µg/L
Bromide	70	µg/L	1.4	0.997	7.0
	170		1.8	0.985	12
	320		3.0	0.997	16
	470		4.0	0.999	19
pH	6.5	---	0.4	0.953	6.5
	7.5		1.6	0.943	15
	8.2		5.1	0.986	16
	8.5		7.2	0.998	21
Temperature	5	°C	0.5	0.933	15
	10		0.9	0.930	12
	15		1.1	0.986	11
	24		2.1	0.975	10
Alkalinity	20	mg/L as CaCO ₃	1.0	0.977	6.5
	50		1.4	0.985	15
	100		1.9	0.982	19
	200		1.9	0.985	23
Ammonia	0	mg-N/L	2.6	0.995	14
	0.17		1.7	0.985	16
	0.51		1.4	0.992	14
	0.85		1.3	0.968	10
DOM	3	°C	2.5	0.993	29
	3.5		2.3	0.998	26
	4		2.1	0.930	26
	4.5		1.9	0.960	25

Table 5.7- Effect of water quality parameters on R_{CT} values and Rate of BrO_3^- formation for CRW water ozonation (baseline conditions: O_3 : 3 mg/L; Br^- : 170 $\mu\text{g}/\text{L}$; pH 7.5; Temperature: 24 $^{\circ}\text{C}$; Alkalinity: 100 mg/L as CaCO_3 ; DOC: 3 mg/L, O3: 4.5 mg/L for DOM experiments).

Parameters	Values	Units	R_{CT} , fast	Rate of BrO_3^- Formation	R_{CT} , slow	Rate of BrO_3^- Formation
			0-2 min ($\times 10^8$)	0-2 min ($\mu\text{g}/\text{L}/\text{min}$)	2-20 min ($\times 10^8$)	2-20 min ($\mu\text{g}/\text{L}/\text{min}$)
Bromide	70	$\mu\text{g}/\text{L}$	3.2	6.0	1.3	1.0
	170		2.2	12.3	0.8	1.2
	320		1.5	13.9	0.6	1.7
	470		1.0	14.5	0.4	2.6
pH	6.5	---	0.6	3.5	0.4	0.5
	7.5		1.5	12.3	0.7	1.4
	8.2		2.9	15.8	1.2	2.6
	8.5		3.6	18.1	1.7	3.5
Temperature	5	$^{\circ}\text{C}$	0.6	5.1	0.2	0.84
	10		0.9	6.3	0.3	1.23
	15		1.2	7.0	0.4	1.4
	24		2.1	10	0.6	1.65
Alkalinity	20	mg/L as CaCO_3	4.7	4.2	2.5	0.7
	50		4.3	10	2.2	0.9
	100		3.2	13.6	1.4	1.1
	200		2.0	15	0.9	1.8
Ammonia	0	mg-N/L	1.8	12.2	0.7	2.5
	0.17		1.8	10	0.7	1.9
	0.51		1.9	8	0.8	1.3
	0.85		1.8	7	0.9	1.0
DOM	3	$^{\circ}\text{C}$	1.3	22	0.5	3.4
	3.5		1.6	20	0.6	3.0
	4		2.1	16	0.8	2.4
	4.5		2.4	14	1.1	1.4

Table 5.8- Summary of relationship among the parameters, R_{CT} and bromate formation for CRW water ozonation (baseline conditions: O_3 : 3 mg/L; Br^- : 170 μ g/L; pH 7.5; Temperature: 24 °C; Alkalinity: 100 mg/L as $CaCO_3$; DOC: 3 mg/L, O_3 : 4.5 mg/L for DOM experiments).

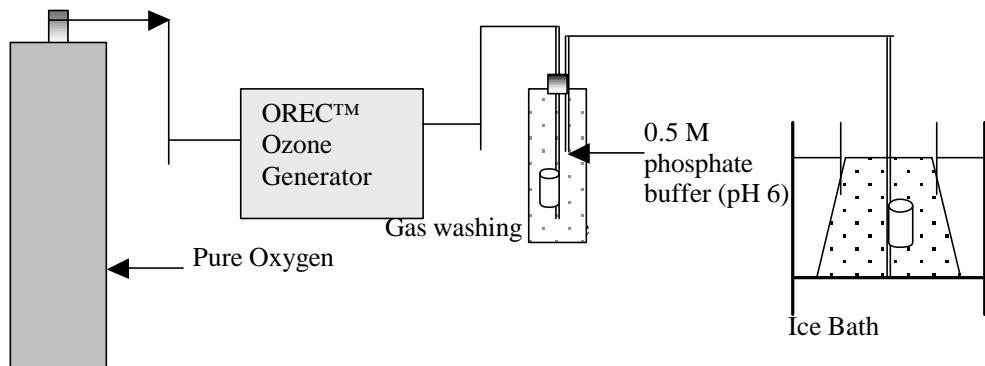
Parameter	Values	R_{CT}	Rate of bromate formation	R^2 for R_{CT} , fast	R^2 for R_{CT} , slow
Bromide	+	-	+	0.91	0.75
pH	+	+	+	0.90	0.99
Temperature	+	+	+	0.99	0.92
Alkalinity	+	-	+	0.80	0.88
Ammonia	+	unchanged	-	0	0
NOM	+	+	-	0.99	0.99



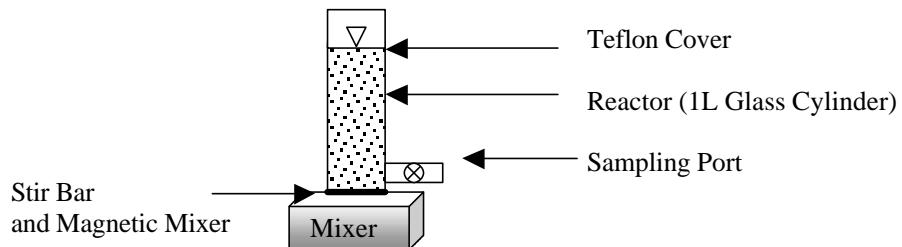
Note: (1) blue and red solid lines represent ozone reaction and blue and red dashed lines represent HO• reaction;

- (2) : Represents direct pathway
 (3) : Represents direct/indirect pathway
 (4) : Represents indirect/direct pathway
 (5) : Represents indirect pathway

Figure 5.1 - Schematic representation of bromate formation by molecular ozone and hydroxyl radicals (von Gunten and Hoigne, 1994).



(a) Stock ozone generator.



(b) Batch ozonation reactor.

Figure 5.2- Schematic layout of (a) stock ozonation generation system and (b) batch ozonation reactor.

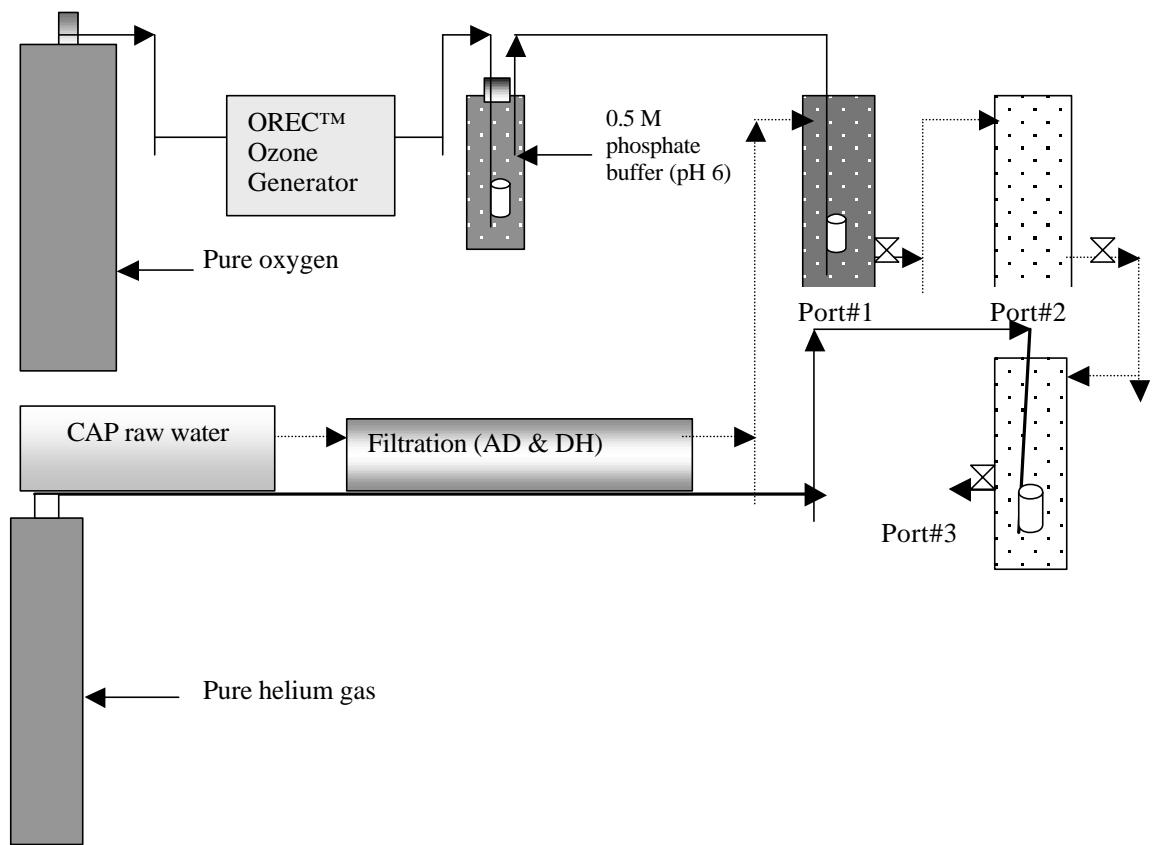


Figure 5.3- Schematic layout of continuous flow ozonation unit (dashed arrows represent water flows during continuous flow ozonation experiments).

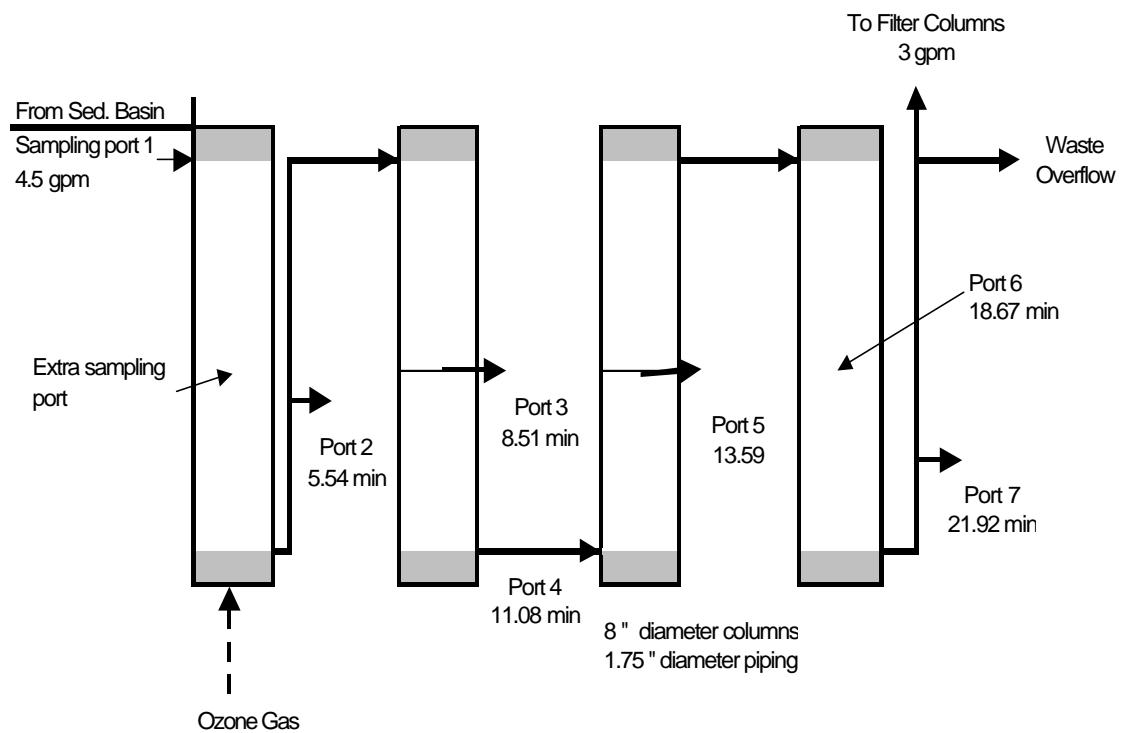


Figure 5.4- Schematic layout of pilot-scale ozone contactor columns with sample port location and cumulative residence time.

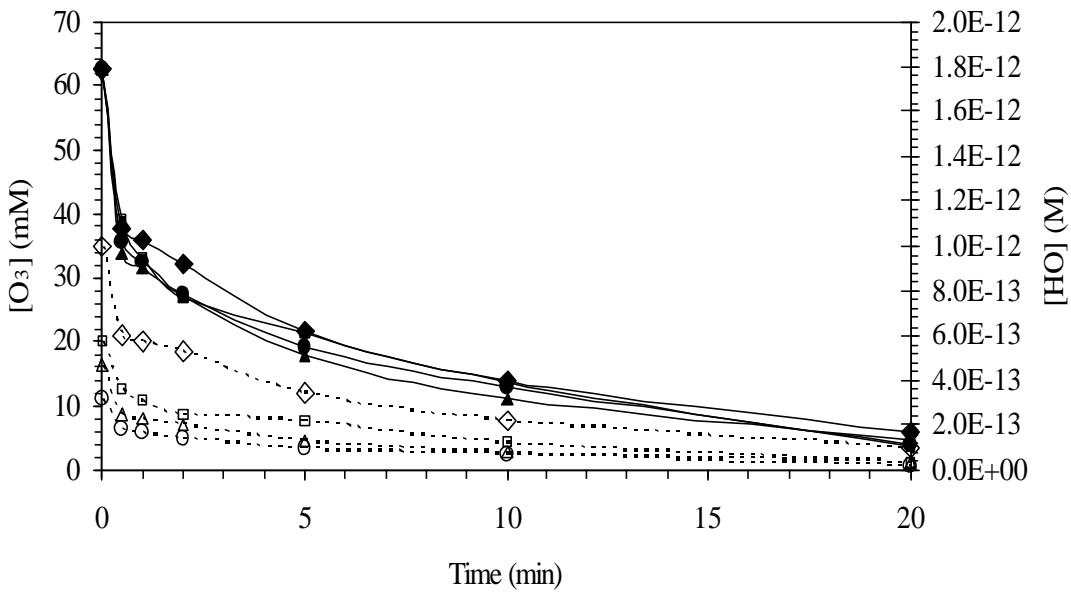


Figure 5.5- Ozone (solid symbols) and HO radical (open symbols) concentrations over time during batch ozonation experiments examining effect of bromide (conditions: O₃: 3 mg/L; pH: 7.5; temperature: 24°C; DOC: 3 mg/L; alkalinity: 105 mg/L as CaCO₃, diamond symbols: 70 µg-Br/L, square symbols: 170 µg-Br/L, triangle symbols: 320 µg-Br/L, circle symbols: 470 µg-Br/L).

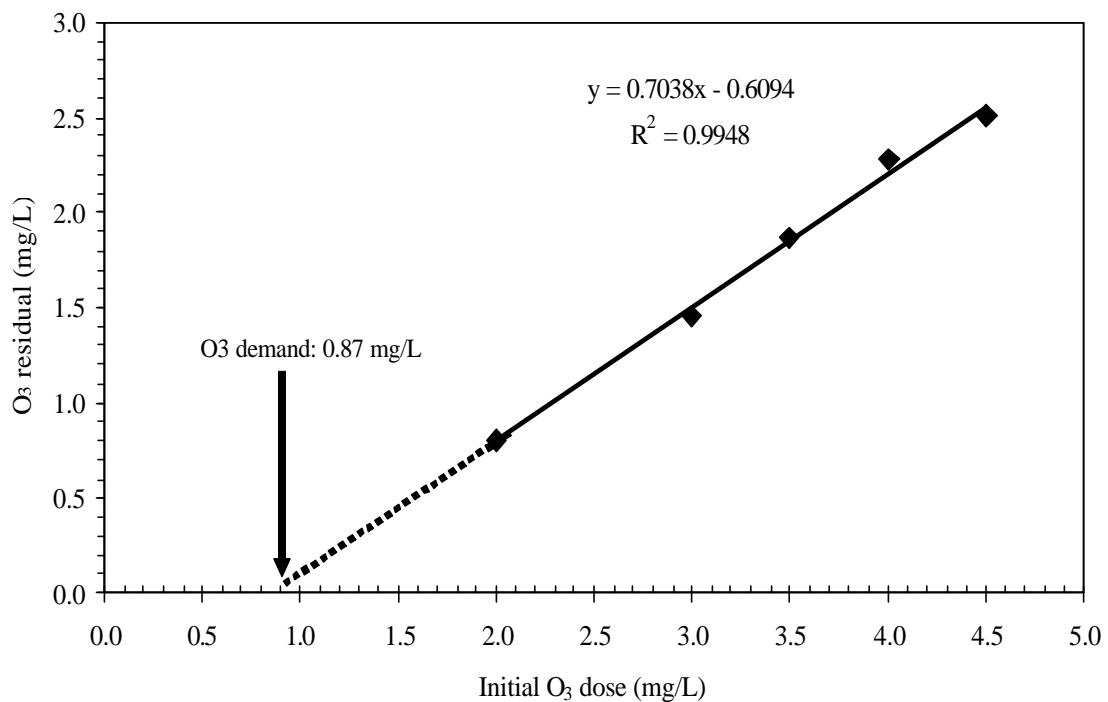


Figure 5.6- Raw CRW water ozone demand curve (conditions: temperature: 24 °C, pH 7.5).

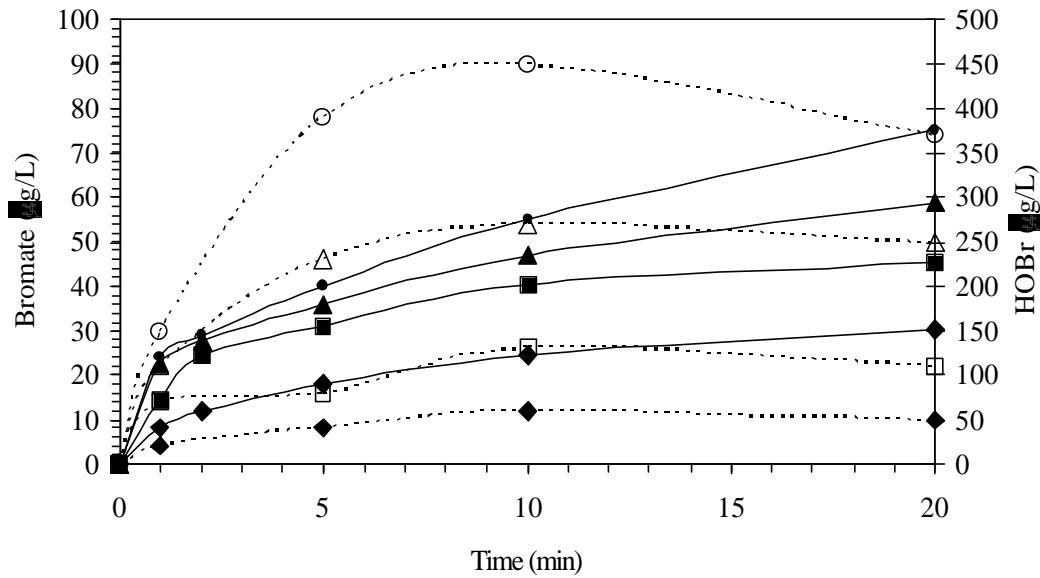


Figure 5.7- Bromate formation and aqueous bromine concentrations over time during batch ozonation experiments examining effect of bromide (conditions: O_3 : 3 mg/L ; pH: 7.5; temperature: 24°C; DOC: 3 mg/L ; alkalinity: 105 mg/L as CaCO_3 , diamond symbols: 70 $\mu\text{g-Br/L}$, square symbols: 170 $\mu\text{g-Br/L}$, triangle symbols: 320 $\mu\text{g-Br/L}$, circle symbols: 470 $\mu\text{g-Br/L}$).

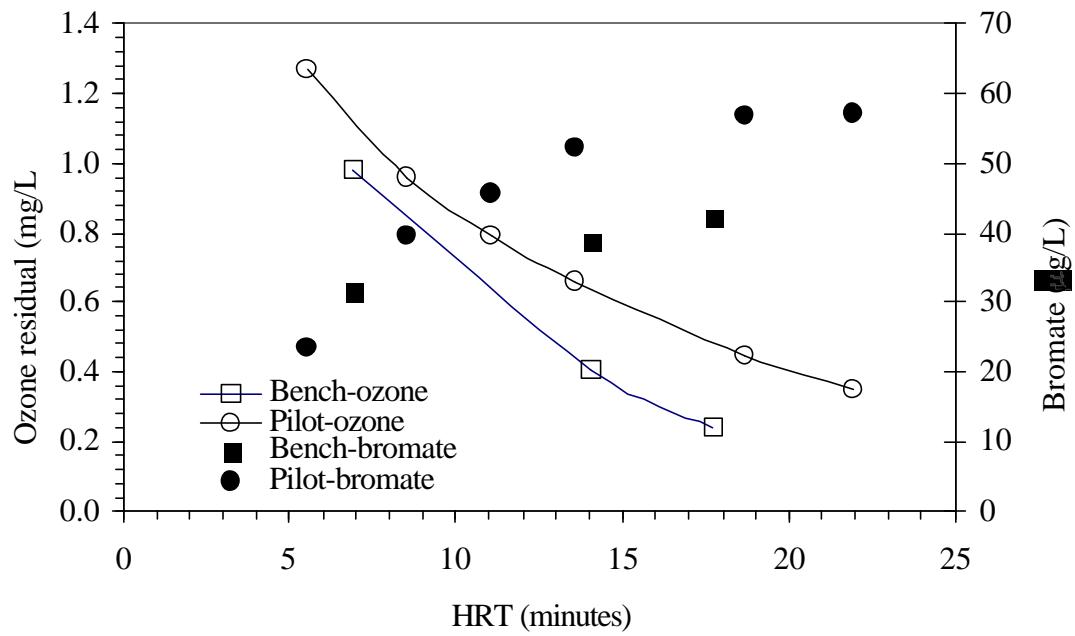


Figure 5.8- Ozone residual (open symbols) and bromate formation (closed symbols) over time in bench- and pilot-scale ozonation experiments (conditions: bromide: 170 µg/L; temperature: 24°C)

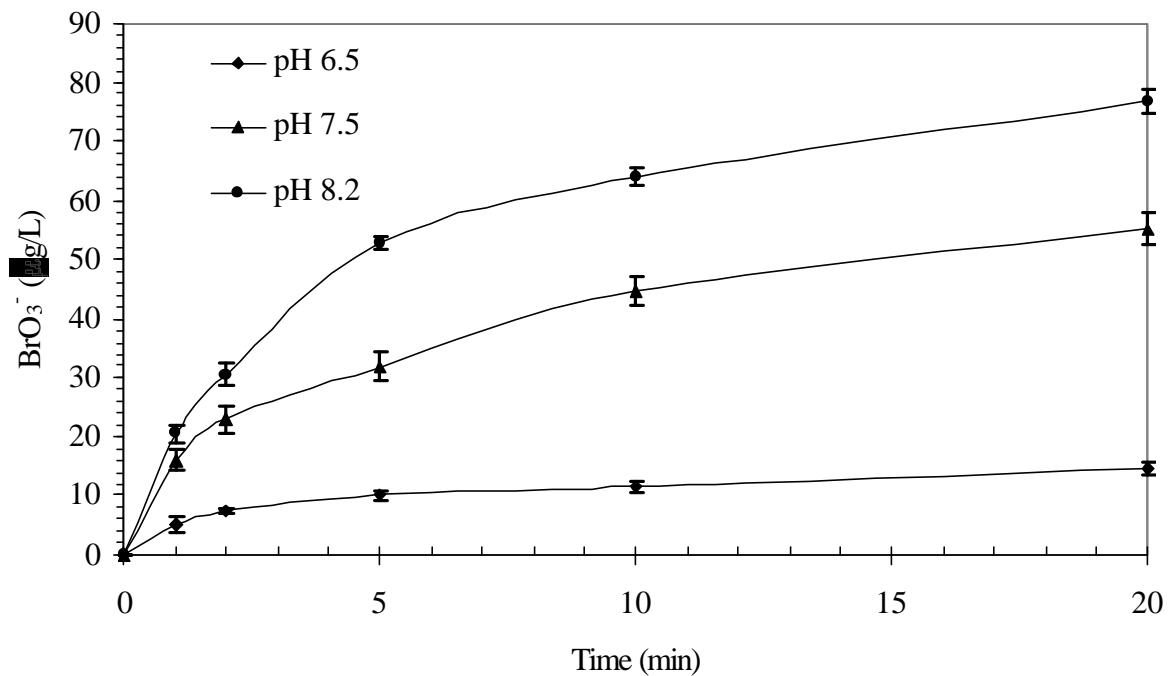


Figure 5.9- Effect of acid addition on bromate reduction in batch ozonation experiments (conditions: O_3 : 3 mg/L; bromide: 170 $\mu\text{g/L}$; temperature: 24°C; error bars represent standard deviations of triplicate experiments).

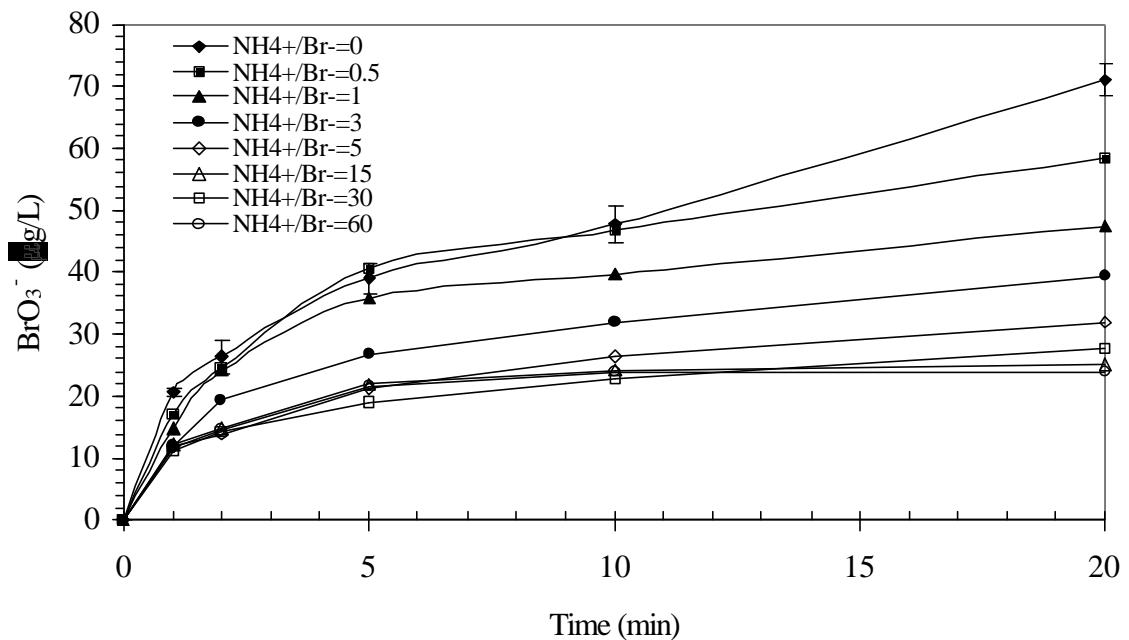


Figure 5.10- Ammonia addition (molar ratios) of bromate reduction in batch ozonation experiments (conditions: O_3 : 3 mg/L, pH 7.5, temperature: 24 °C, Br^- = 170 $\mu\text{g/L}$).

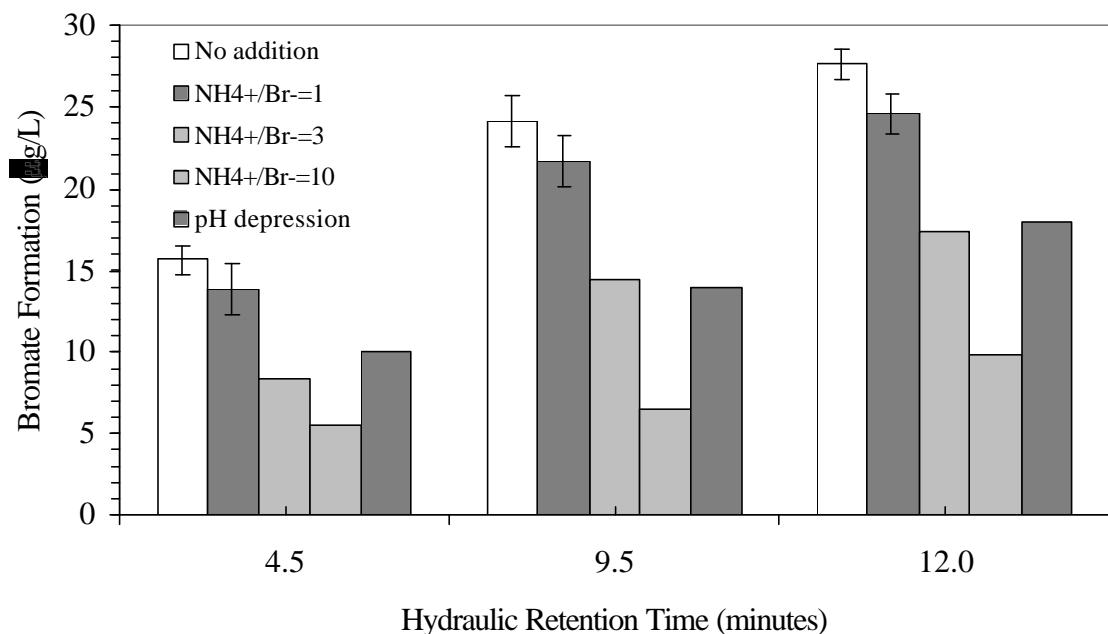


Figure 5.11- Addition of ammonia at various dose and acid on bromate reduction in bench-scale continuous flow ozonation (conditions: [NH₃-N]: 0.03, 0.09, 0.3 mg/L, pH decrease: 8.2 to 7).

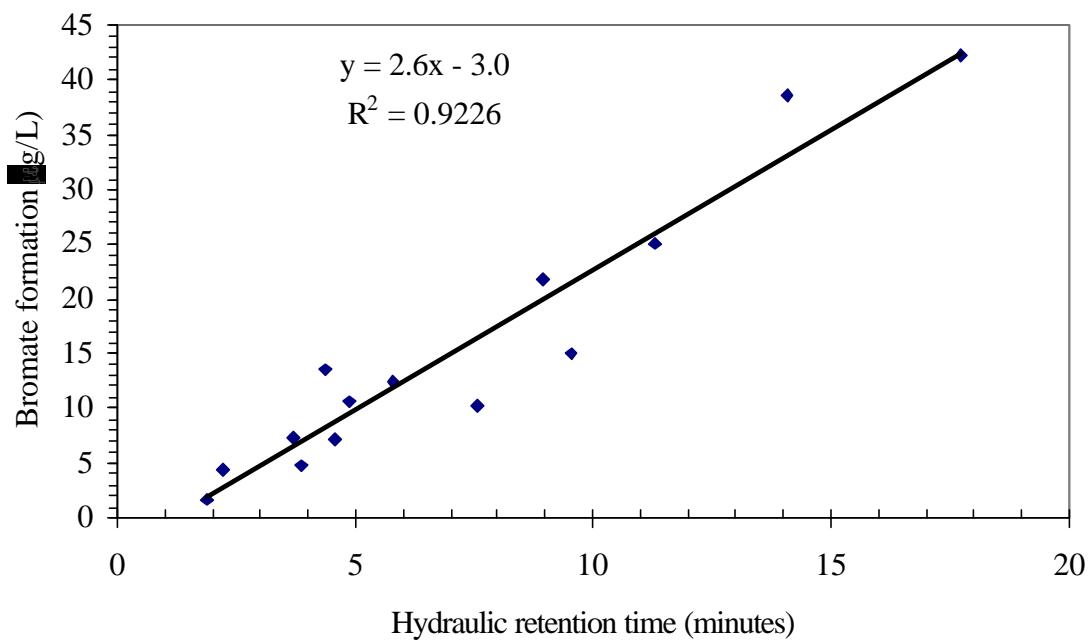


Figure 5.12- Relationship of bromate formation and hydraulic retention time in bench-scale continuous flow ozonation (conditions: bromide: 70 µg/L; pH: 7.5; temperature: 24°C, water flow: 0.14 L/min to 0.55 L/min).

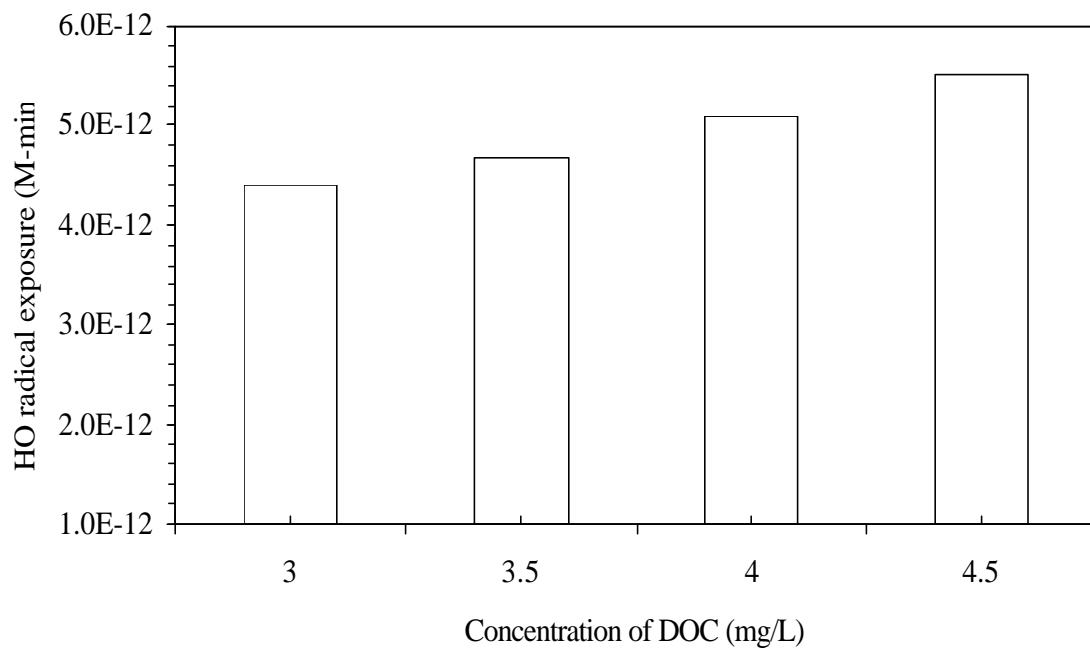


Figure 5.13- Effect of CRW DOC on HO radical exposure in batch ozonation (conditions: O₃: 4.5 mg/L, pH 7.5; temperature: 24 °C).

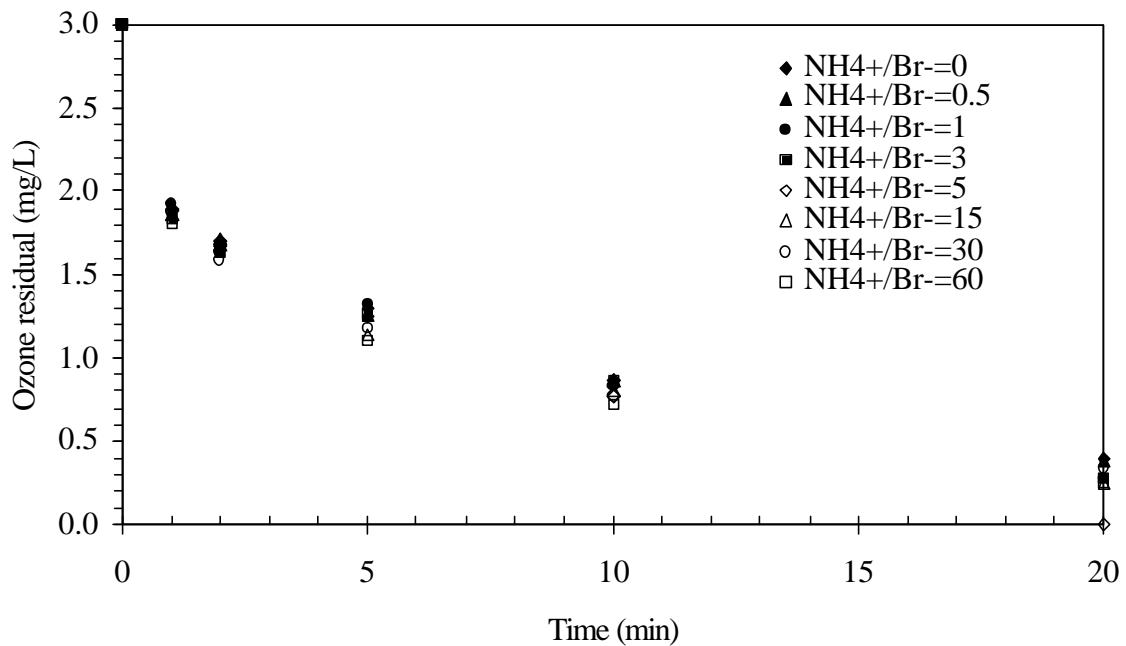


Figure 5.14- Ozone decomposition over time during ozonation experiments at various dosages of ammonia in term of $\text{NH}_4^+/\text{Br}^-$ molar ratios (conditions: O_3 : 3 mg/L; pH 7.5; temperature: 24 °C).

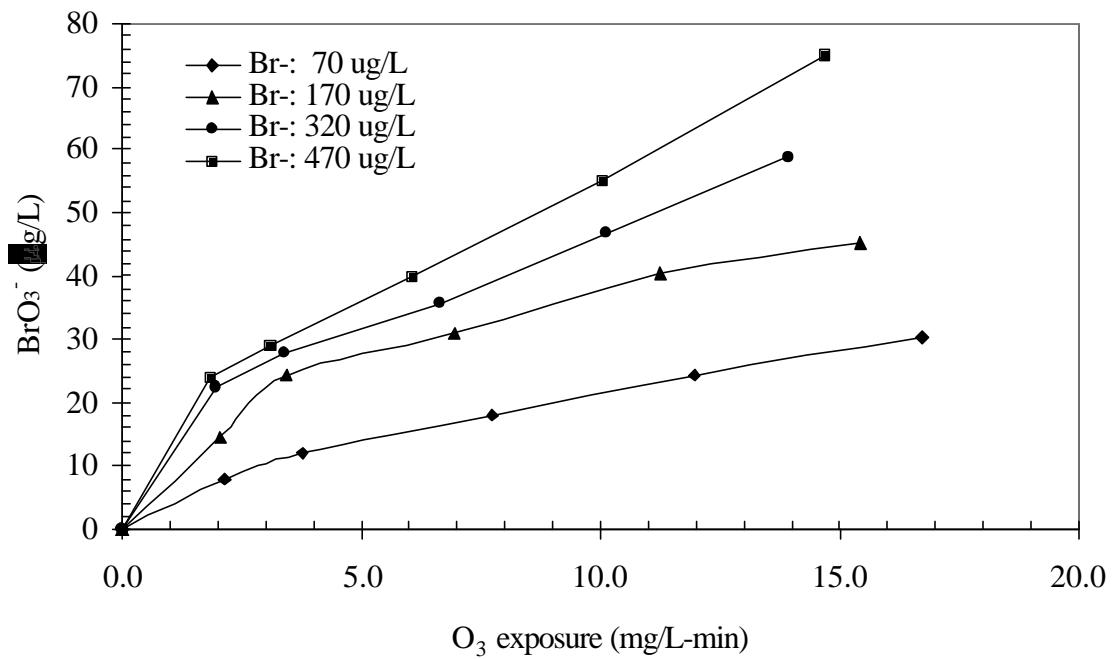


Figure 5.15- Bromate formation versus integrated ozone exposure in batch ozonation experiments examining bromide effect.

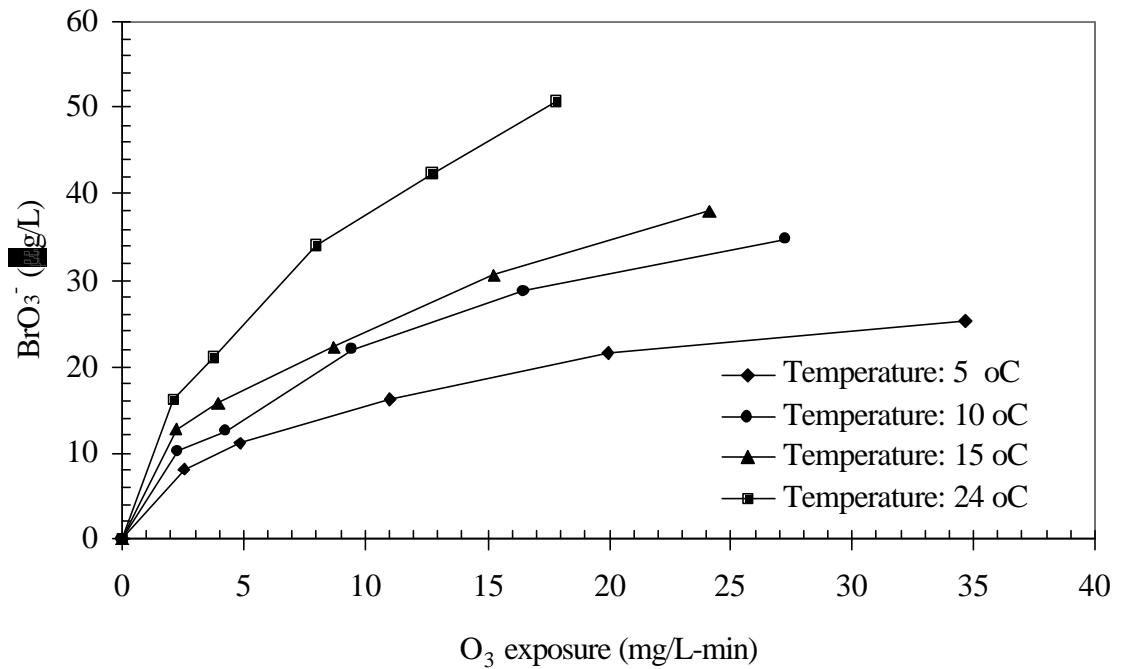


Figure 5.16- Bromate formation versus integrated ozone exposure in batch ozonation experiments examining temperature (in Celsius) effect.

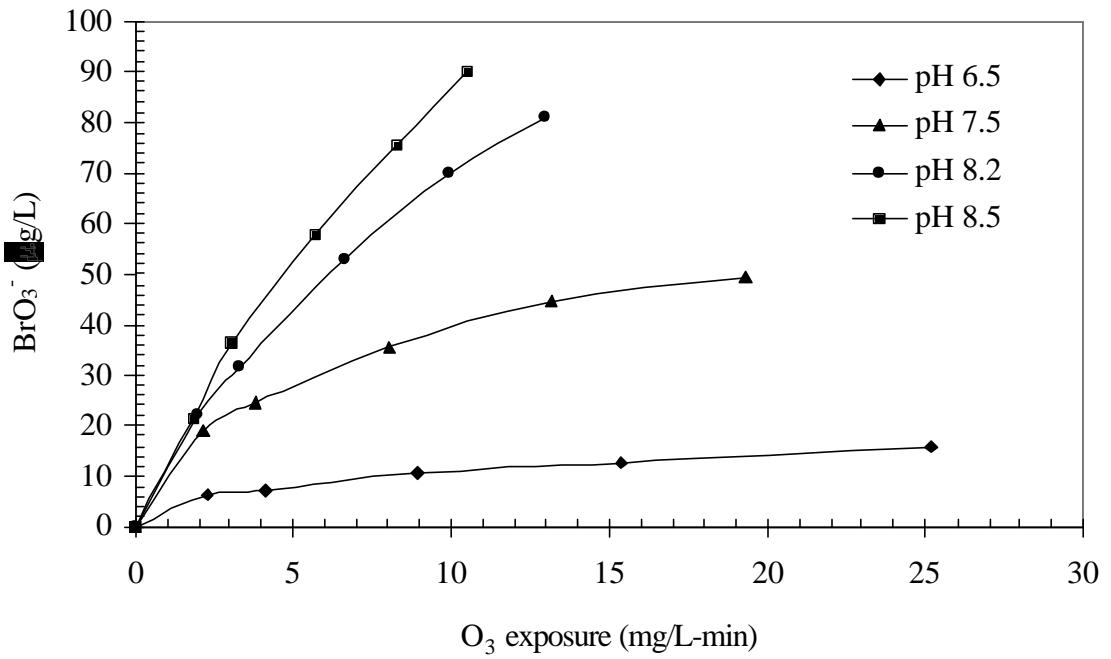


Figure 5.17- Bromate formation versus integrated ozone exposure in batch ozonation experiments examining pH effect.

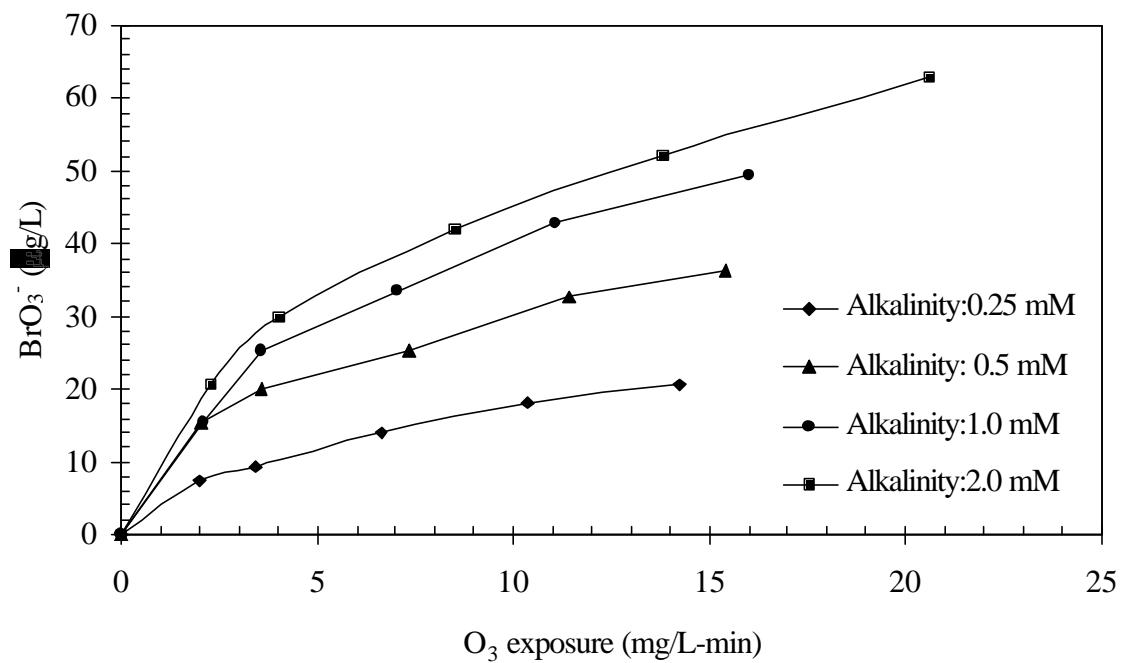


Figure 5.18- Bromate formation versus integrated ozone exposure in batch ozonation experiments examining (bi)carbonate alkalinity effect.

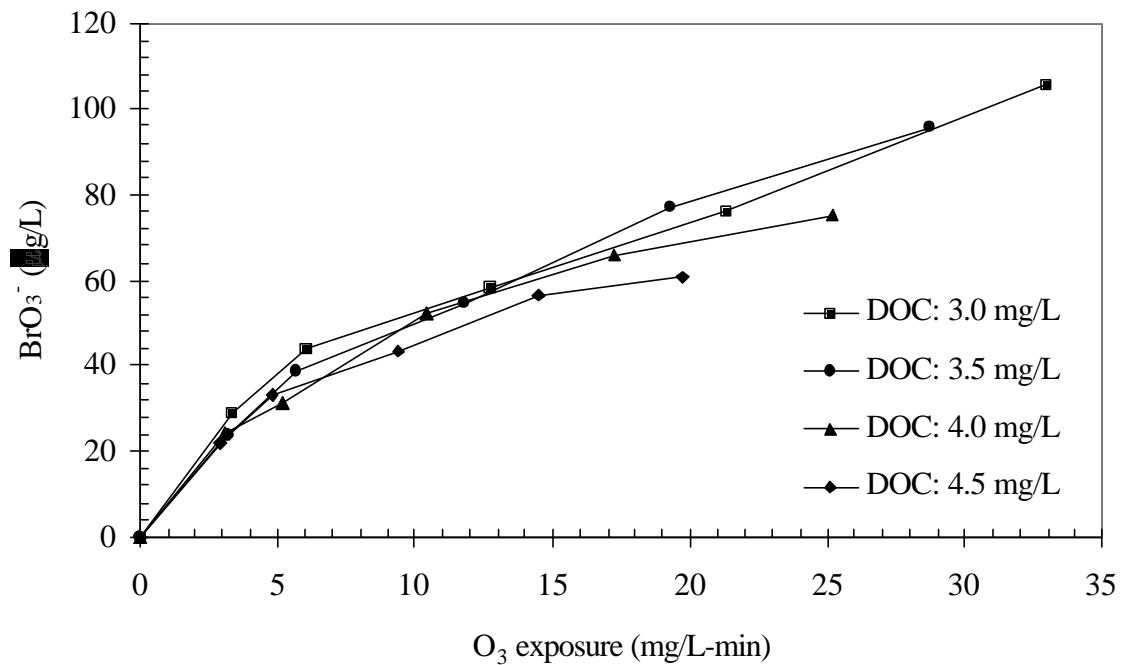


Figure 5.19- Bromate formation versus integrated ozone exposure in batch ozonation experiments examining DOC effect.

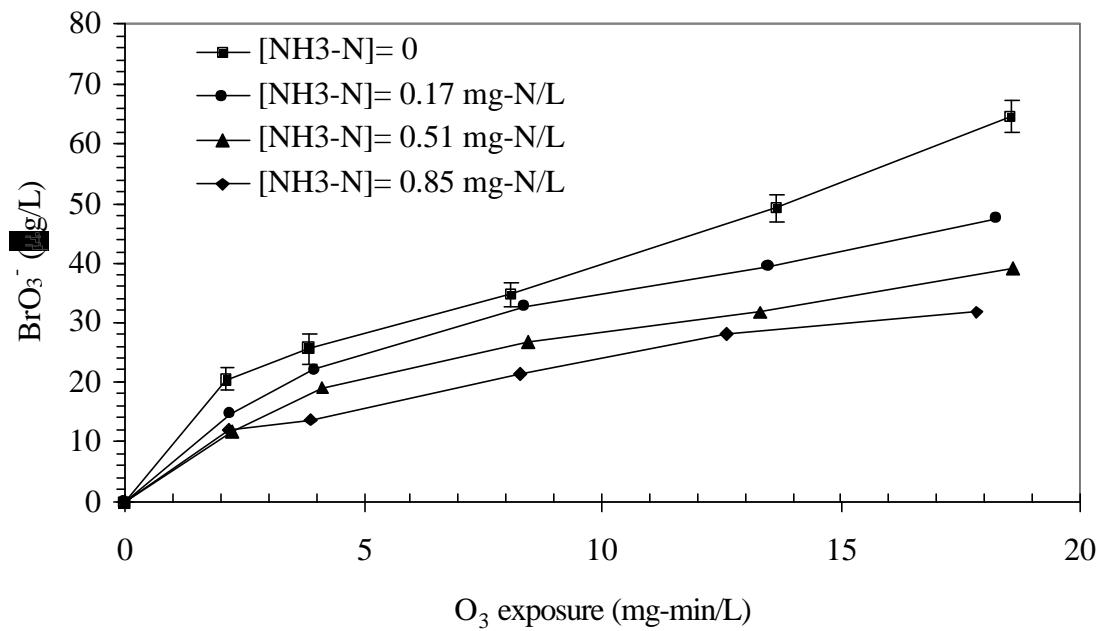


Figure 5.20- Bromate formation versus integrated ozone exposure in batch ozonation experiments examining ammonia effect.

15. CHAPTER 6

16. KINETIC ASPECTS OF BROMATE MINIMIZATION BY AMMONIA DURING OZONATION OF BROMIDE CONTAINING WATERS

16.1. 6.1 INTRODUCTION

Bromate ion (BrO_3^-) does not usually occur in raw drinking waters, but it can be easily formed in ozonated waters in the presence of bromide ion (Br^-). Although some chemical solutions such as sodium hypochlorite (NaOCl) used for industrial purpose can contain residual bromate, the major concern of bromate occurrence in drinking water sources is that when waters are treated by ozone. Bromate is strictly regulated due to its suspected human carcinogenic toxicity. Based on the current limitation of detection technology and the priority of safe water disinfection, the United States Environmental Protection Agency (USEPA, 1998a) regulated the maximum contamination level (MCL) of bromate in drinking water in the Stage I Disinfectant/Disinfection By-Product Rule (D/DBP R) at 10 $\mu\text{g/L}$, which poses a health risk of slightly greater than 10^{-5} (EPA, 1998b).

A number of possible methods to control formation of bromate during ozonation have been proposed including 1) reduction of initial water bromide levels, 2) scavenging HO radicals (HO^\bullet) in which formed as ozone decomposition by-products that can oxidize bromide to bromate, 3) lowering intermediate hypobromite ions (OBr^-) during ozonation, and 4) removal of bromate after ozonation. Attempts to physically or chemically reduce bromate's precursor, bromide ion, existing in waters tend to be impractical and efforts to remove once formed bromate from ozonated water could be cost ineffective or impractical (Asami et al., 1999, Amy et al., 1997). Therefore, the focus of treatment strategies should be on preventing the formation of bromate.

In drinking water treatment, the reduction of intermediate OBr^- concentration by decreasing water pH and/or addition of ammonia is probably the most applicable option in controlling bromate formation (Pinkernell and von Gunten, 2001). However, the method of pH depression to control bromate formation might cause corrosion problems, and for waters with high (bi)carbonate alkalinity, adding large amounts of acid to control bromate formation below the MCL might not be economical. On the other hand, it has been demonstrated that the presence of ammonia can reduce bromate formation during ozonation processes

(Haag et al., 1984; Hoigne et al., 1993; Song et al., 1997; Hofmann and Andrews, 2001; Pinkernell and von Gunten, 2001). Recent studies conducted by several researchers (Hofmann and Andrews, 2001; Pinkernell and von Gunten, 2001) showed that even a small amount of ammonia led to significant reduction of bromate compared to waters without ammonia during ozonation.

The goal of this study is to investigate the effect of ammonia on bromate reduction as well as on the effect of ozone disinfection (e.g., ozone exposure and HO[•] exposure). Chapter 4 described that the relationships of R_{CT}, representing the ratio of HO[•] exposure (or concentration) and O₃ exposure (or concentration), is independent of ammonia addition. Whereas Chapter 5 identified pH and ammonia, separately, as viable bromate controls, very little published data is available on optimizing simultaneous acid and/or ammonia addition for bromate control. The optimization of bromate reduction on addition of ammonia at various pH ranges was therefore evaluated. It is hypothesized (*Hypothesis III*) that “*ammonia addition for controlling bromate formation does not alter the [HO[•]]/[O₃] ratio, but shifts bromate formation towards the HO[•] oxidation pathway by scavenging HOBr/OBr[−]*“.

16.2. 6.2 BACKGROUND

Bromate control by ammonia is based upon the bromate formation pathways (O₃ or HO[•] pathways) that involve the intermediate hypobromous acid (HOBr), where nonionic species of ammonia will rapidly scavenge HOBr rather than allowing its conjugate base, OBr[−], to continue to react with O₃ and HO[•] and the reaction is shown below (Wajon and Morris, 1979):



Meanwhile, ammonia can also react with OBr[−] releasing bromide and nitrogen gas (LaPointe, et al., 1975):



Equation 6-2, however, is the net reaction, and does not describe the true reaction mechanism. Based upon the stoichiometric of the reaction, the fastest reaction rate occurs at the N:Br ratio of 2:3 and decreases as the ratio deviates (Johnson and Overby,

1971; LaPointe et al., 1975). Some studies, however, had indirectly demonstrated that there was no ammonia loss to nitrogen gas (Haag et al., 1984; von Gunten and Hoigne, 1994), which implied that the reaction was not thermodynamically favorable. Compared with the dominant reaction shown in Equation 6-1, the reaction of OBr^- and NH_3 can, therefore, be neglected during ozonation.

The reduction of free bromine (e.g., HOBr/OBr^-) by ammonia prevents further oxidation by ozone or HO^\bullet to form bromate. However, bromate formation via bromide oxidation by HO^\bullet without the formation of HOBr or OBr^- occurs (von Gunten and Hoigne, 1994). Therefore, in combination with both molecular ozone and HO^\bullet , a number of possible bromate formation pathways are shown in Figure 6.1 (von Gunten and Hoigne, 1994). In addition, the presence of both bicarbonate and carbonate ions in the waters are capable of scavenging HO^\bullet and form secondary inorganic carbonate radicals ($\text{CO}_3^{\cdot-}$). These active carbonate radicals can oxidize OBr^- and BrO_2^- and form bromate precursors, e.g., BrO^\bullet or $\text{BrO}_2^{\cdot-}$ (Buxton, et al., 1988). The BrO^\bullet or $\text{BrO}_2^{\cdot-}$ will then disproportionate and form more bromate (von Gunten and Hoigne, 1994). Song et al. (1996) critically reviewed existing bromate formation models and performed bench-scale experiments to elucidate that bromate formation in ozonation was via three major pathways, which left the indirect HO^\bullet pathway neglected (Figure 6.2). Both of the direct (D) and direct-indirect (D/I) pathways of bromate formation are involved intermediate HOBr/OBr^- ; therefore, the presence of ammonia can alter reaction pathways to form bromamines (e.g., NH_2Br , NHBr_2 , and NBr_3) and thus reduce bromate formation. However, it is expected that ammonia cannot guarantee reducing overall bromate since

the I/D pathway may contribute to the formation of bromate by oxidizing bromide ion via Br[•] and BrO[•] radicals.

Based upon the reaction of ammonia and hypochlorous acid reported by Weil and Morris (1949) and similar physical and chemical properties of hypochlorous acid and hypobromous acid, a second-order kinetic rate expression was shown as follow (Wajon and Morris 1979):

$$R = k_{\text{NH}_3,\text{HOBr}} [\text{NH}_3][\text{HOBr}] \gamma_{\text{NH}_3} \gamma_{\text{HOBr}} / \gamma_x \quad 6-3$$

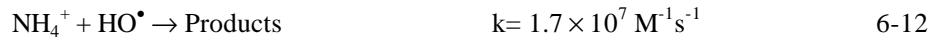
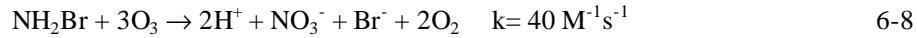
where R represents the rate of reaction of ammonia and HOBr, $k_{\text{NH}_3,\text{HOBr}}$ is the rate constant, and γ is the activity coefficient (γ_x represents the activated complex). Since both of the concentrations of NH₃ and HOBr are in diluted conditions, the values of γ_{NH_3} , γ_{HOBr} , and γ_x are approximately equal to 1. Equation 6-3 shows that deprotonated form (NH₃) of ammonia species is more activated than NH₄⁺, thus reaction is favored at high pH. On the other hand the protonated form (HOBr) of bromine species is more activated than OBr⁻, and thus reaction is favored at low pH (Wajon and Morris, 1979). Since the equilibrium constant (K_a) for HOBr and OBr⁻ is 8.86 at 20 °C (Haag and Hoigne, 1980; Westerhoff, 1995) and K_a for NH₄⁺ and NH₃ is 9.3 (Snoeyink and Jenkins, 1980), it is expected that rate reaction is a function of water pH. In addition, three species of ammoniacal bromamines are formed by the stepwise addition of bromine to ammonia (Galal-Gorchev and Morris, 1965). The stoichiometric equilibrium constants and estimated free energies at 20 °C are shown below (Sugam, 1977; Sugam and Helz, 1981):



The large positive free energies indicate that these compounds are likely to be thermodynamically unstable. It has been reported that the ratio of the three species of bromamines (e.g., NH₂Br, NHBr₂, and NBr₃) are dependent on pH and the ratio of HOBr to NH₄⁺-N (Johnson and Overby, 1971). Despite the coexistence of these bromamine species, under typical ozonation conditions using ammonia to control bromate (e.g., pH 6-9 and NH₃ > Br⁻), NH₂Br is the only dominating species.

Addition of ammonia to reduce bromate formation during the ozonation process, however, has its limitations. Ammonia can only control bromate formation through two of the three pathways (shown in Figure 6-2) that involve HOBr as a significant intermediate. Ammonia, however, can also react with

molecular ozone or HO[•]. Once ammonia is depleted, bromate formation can resume via all the pathways. The following shows possible reactions, which consume ammonia, including Equation 6-1 (Hoigne and Bader, 1983 II & III):



It appears that among the above reactions only Equation 6-1 is probably the dominant reaction to consume ammonia during ozonation when both bromide and ammonia concentrations are low (e.g., < 1 mg/L). Equations 6-1 and 6-8 show that the intermediate by-product of bromide oxidation, hypobromous acid, can quickly react with ammonia to form monobromamine, which in turn releases bromide upon oxidation of ozone. As a result, ammonia is consumed via this cyclic process that is catalyzed by bromide (Haag et al., 1984). This could explain observation from a study conducted by Krasner et al. (1993) who reported that ammonia addition did not control bromate formation in several pilot plants. Instead, addition of ammonia could only delay bromate formation during continuous flow ozonation process.

16.3. 6.3 METHODOLOGY

Bench-scale batch and continuous flow ozonation experiments were conducted in the laboratory. Details of materials and methods used for this study are described below:

Materials: All chemicals added were analytical grade and stock solutions for adjusting initial water qualities were prepared with water (>18mΩ) made from ultrapure water system (Namopure Infinity™). Gaseous ozone was generated by ORECTM (Model V5-0, Phoenix, AZ) ozone generator from pure oxygen (99.999%). Figure 6.3 shows the schematic diagram of stock ozone solution generation for batch experiments. The concentrated dissolved O₃ stock solutions were produced by continuously bubbling

pure gaseous O₃ through a two-liter glass reactor filled with Nanopure-water that was cooled in an ice bath. Gaseous ozone was transported by stainless steel tubing and passed a gas-washing bottle containing 0.5 M phosphate buffer (pH 6) to remove nitric oxidized impurities before dissolving into water. A saturated stock O₃ solution of approximately 40 mg/L (based on UV absorbance's molar extinction coefficient of ε_{258nm} = 3150 M⁻¹ cm⁻¹ @ pH 2) was achieved routinely after an hour.

All experiments were performed with one the same source water from the Colorado River conveyed by the Central Arizona Project canal (CRW water). The raw CRW water used for batch and continuous flow experiments was collected at the Scottsdale Water Campus in Scottsdale, Arizona. Waters used for batch experiments were passed through pre-ashed glass filter papers (GF/F WhatmanTM) to remove particles. Filtered water was stored at 4 °C before use. The pH of all waters was adjusted to the desired values by adding prepared stock solutions of sulfuric acid or sodium hydroxide. Since the collected CRW water contained very low ammonia concentration (< 10 µg/L), ammonium chloride was used to adjust ammonia levels in the water. All water samples were spiked with 0.25 µM of para-chlorobenzoic acid (PCBA) before ozonation to measure HO[•] concentration.

Batch Ozonation Experiments. Batch ozonation experiments were performed by injecting small volumes of the ozone stock to achieve desired ozone concentrations in a 1-L cylinder reactor (Figure 6.3) containing 500 milliliters of prepared waters with adjusted water quality. A Teflon mesh was applied to cover the top of water surface as soon as stock ozone solution was added to prevent ozone loss by volatilization. Samples were collected over time to monitor residual ozone by the indigo method (Bader and Hoigne, 1981) and for PCBA, HOBr, bromate and nitrate analyses. The collected samples were immediately bubbled with high flow of pure helium (99.999%) to remove ozone residual.

Continuous-flow Ozonation Experiments. The gaseous ozone with adjusted flow rate passed through the first 500-mL gas-washing bottle with 0.5-M phosphate solution (pH 6) and then the pure gaseous ozone was introduced to the bottom of the first 1-L reactor with a diffuser, whereas the countercurrent filtered (0.1 µm AH & DH, WhatmanTM) CRW water with various flow rates flowed into the reactor from the top port (Figure 6.4). Ozone residuals at different sampling ports, which representing different hydraulic retention times, were monitored. When ozone concentrations remained constant over time (reached a steady state condition), water samples were collected at sampling ports 1, 2 and 3 and then

ozone residuals were stripped off with helium immediately for later bromate, nitrate and PCBA analyses. Based upon the determined water flow rate of 0.2L/min, the hydraulic retention times (HRTs) for the three reactors are 4.5, 9.5 and 12 minutes, respectively. Detailed results of trace tests are shown in Appendix B.

Analytical Methods. The dissolved NOM-free O₃ concentrations in the stock solution were determined by the direct UV absorbance at wavelength 258nm ($\epsilon = 3150 \text{ M}^{-1}\text{cm}^{-1}$) (Langlais et al., 1991). Stock O₃ solution was diluted to an UV absorbance of less than 1.0 cm⁻¹ with diluted phosphoric acid to remain in the linear portion based upon Beer's Law. For waters containing natural organic matter (NOM), dissolved O₃ residual was measured with ShimadzuTM UV/Vis spectrophotometer using the indigo colorimetric method (Bader & Hoigne, 1981). Solution pH and temperature were measured using a BechmanTM pH electrode, which was calibrated with standard buffers (J. T. BakerTM). Aqueous bromine (HOBr/OBr⁻) was measured using HachTM pocket colorimetric spectrophotometer. Bromide, bromate and nitrate were measured using a DionexTM ion chromatography. The system included an anion self-regenerating suppressor and conductivity meter and the columns used included a DionexTM AG9-HC guard column to prevent potentially fouling the AS9-HC analytical column. The analytical method included a 9.0-mM sodium carbonate, 1.0-mL/min flow rate, and a 500-μL injection loop. Bromate samples were pretreated to remove the abundant chloride ion (Cl⁻) existing in CRW water using DionexTM OnGuard-Ag and -H cartridges (for removing residual Ag) connected in series since in ion chromatograph the Cl⁻ peak is adjacent to BrO₃⁻ and high Cl⁻ concentration results in the overlap of BrO₃⁻ peak. PCBA was determined using a WatersTM high performance liquid chromatography (HPLC) with a reverse-phase (RP-18) analytical column, a 500-μL injection loop and 1.0-mL/min flow rate of mobile phase consisting of a mixture of 55% methanol and 45% 10 mM phosphoric acid. Detection was made using an UV detector set to a wavelength of 234 nm.

16.4. 6.4 RESULTS

16.4.1. 6.4.1 Ozone Decomposition

The results from both batch and continuous flow ozonation experiments show that ozone decomposition rates remain unchanged in the presence of low ammonia concentrations (in ppb levels). Figure 6.5 shows that no measurable change of ozone residuals over time at various levels of ammonia less

than 32 μM (0.5 mg-N/L) in batch experiments that held other parameters constant. However, when ammonia concentration was increased to 128 μM , an approximately 10% decrease of ozone residuals was observed. Based upon bromate reduction efficiency from batch experiments (shown in Section 6.3.3), dosages of ammonia addition were defined as low, intermediate, and high levels, which were represented by molar ratios of $\text{NH}_4^+/\text{Br}^-$ of 1, 3, and 10, respectively. These three ammonia dosages were applied to continuous flow ozonation experiments. As shown in Figure 6.6, residuals of ozone remained nearly unchanged at three different sample locations.

16.4.2. 6.4.2 Determination of $[\text{HO}^\bullet]/[\text{O}_3]$

As discussed previously in Chapter 4, the value of R_{CT} , defined as ratio of $[\text{HO}^\bullet]/[\text{O}_3]$, is calculated from the slope of the plot of the natural logarithm of PCBA concentration against ozone exposure. Table 6.1 and Table 6.2 summarize the calculated R_{CT} values in batch and continuous flow ozonation experiments at various ammonia concentrations. Table 6.1 shows two R_{CT} values for each batch experiment, representing a two-stage ozonation (fast and then slow stages). The values of R_{CT} at fast stages are always higher than at slow stages and are approximately by a factor of 2. However, due to the experimental setup, only a slow stage ozonation process was observed in continuous flow experiments. In general, R_{CT} values increase with increasing pH, but remain almost unchanged if the amount of added ammonia is less than 32 μM . Based upon the known ozone data, the concentrations of HO^\bullet (or $\int \text{HO}^\bullet dt$) at a specific time was determined by taking the product of ozone concentration at that specific time and multiply by the R_{CT} value. As expected, HO^\bullet (or exposure) is not affected by adding low amount of ammonia.

16.4.3. 6.4.3 Bromate Formation

Bromate formation is reduced as ammonia is added into waters prior to ozonation. However, the effect of ammonia on bromate reduction is dependent upon pH. In batch ozonation experiments, the dosage of ammonia was determined based upon the molar ratio of $\text{NH}_4^+/\text{Br}^-$ multiplying by bromide concentration. Figure 6.7 to Figure 6.9 show kinetic bromate formation at different water pH levels and ammonia concentrations in terms of $\text{NH}_4^+/\text{Br}^-$ molar ratios. After a 20-minute period of ozonation, the

ozone residuals remained approximately 0.35 mg/L and 0.22 mg/L at water pH 6.5 and 7.5, respectively and almost no ozone residual remained at pH 8.5. As expected, bromate formation kinetically increased as increasing water pH. When comparing against the CRW water that has no ammonia addition, the addition of highest ammonia dose (120 μ M) at pH 6.5 resulted in 27 %, 20 %, and 8 % reduction in bromate formation at 5, 10, and 20 minutes ozone exposures, respectively. A similar trend of decreasing bromate reduction efficiency over time was observed to other experiments at pH 6.5 with different ammonia doses.

With increasing pH, bromate reduction efficiency by ammonia addition is enhanced. Even a very small amount of ammonia addition (~10 μ g-N/L) results in measurable difference of bromate when water pH is raised to 8.5 (Figure 6.9). Kinetically, the bromate reduction efficiency increased at higher ammonia doses and longer reaction times in comparison to waters without ammonia addition. When the molar ratio of $\text{NH}_4^+/\text{Br}^-$ is greater than 15, up to 60% and 85% of bromate reduction were achieved at pH 7.5, and 8.5, respectively after 20 minutes. It is observed that maximum reduction of bromate was achieved when the dosage of ammonia, expressed as molar ratio of $\text{NH}_4^+/\text{Br}^-$, is greater than 15. Up to this amount, further slight reduction of bromate resulted from lowering ozone exposure by the significant consumption (> 10% change) of ammonia reaction with ozone.

However, even a very high dose of ammonia was applied, some bromate still formed. It was observed that bromate was formed very rapidly within the first one minute when intermediate free bromine has not started accumulating (data not shown). This observation agrees with a statement by Driedger, et al. (2001) that bromate formation is dominated by the HO^\bullet mechanism during the initial phase. Figure 6.9 shows that when excess amount of ammonia is applied at pH 8.5, the majority of overall bromate is formed within a minute. For example, at a $\text{NH}_4^+/\text{Br}^-$ molar ratio of 60, a 10 μ g/L of bromate formed within 1 minute, representing 75 % of the bromate present after 20 minutes. Rapid ammonia reaction with the once formed intermediate HOBr reduces its conjugated base, e.g., OBr^- , concentration and therefore, blocking further oxidation to bromate. Reduction of bromate over time becomes more effective after two minutes, which is considered as slow-stage of ozonation that the formed OBr^- is immediately reduced by ammonia.

Figure 6.10 shows a similar trend of bromate formation over time for continuous flow ozonation experiments with different dosages of ammonia added into the water prior to the tests. High ambient temperature (24 °C) and pH (8.2) of CRW water resulted in high bromate formation. At HRT of 12

minutes with remaining ozone residual of 0.24 mg/L, approximately 25% of bromide has oxidized to bromate (27.5 µg/L). Addition of ammonia effectively reduced bromate formation. With addition of ammonia doses of 0.9, 2.7, and 9 µM, bromate was reduced by 10%, 35% and 65%, respectively when compared against no ammonia addition at 12 minutes of HRT.

16.4.4. 6.4.4 Intermediate Aqueous Bromine Formation

Intermediate free aqueous bromine (e.g., HOBr and OBr⁻) plays an important role on bromate reduction by adding ammonia during ozonation of waters containing bromide. Aqueous bromine, formed from the oxidation of bromide by ozone, is very reactive to ammonia. In batch ozonation experiments under the baseline conditions (e.g., O₃: 3 mg/L, temperature: 24 °C, pH 7.5, bromide: 2.13 µM), up to 50 % of total of initial bromide was oxidized to bromine. However, the measured free bromine might be underestimated due to analytical setup that the collected samples were purged with pure helium to remove residual ozone before bromine measurement. This removing process of ozone residual results in almost lag time of a minute for the bromine measurement. In addition, although the analytical method calibrated by free chlorine was designated to only measure free aqueous bromine, free bromine concentrations were not to accurately quantify. It appears that using colorimetric DPD method cannot differentiate accurately between free bromine and total bromine (i.e., HOBr/OBr⁻ and the three bromamines) since some bromamine species were still incorporated as free bromine. Figure 6.11 shows measured free bromine concentration over time at various ammonia doses. Waters prior to ozonation always showed low levels of bromine readings, which were considered as background of light absorbance from the indicators. A similar trend was observed that in experiments without any presence of ammonia, free bromine usually started

accumulating in the first 10 minutes followed by gradual degradation afterwards. Experiments with addition of ammonia showed that even though encountering a challenge to differentiate between free and total bromine during the ozonation process, the results show that higher concentrations of accumulating “measured” bromine species were observed during the ozonation processes when adding higher doses of ammonia and, therefore, results in less bromate formation (Figure 6.11).

16.5. 6.5 DISCUSSION

16.5.1. 6.5.1 Effect of Ammonia on Ozone Decomposition

Ammonia can react with molecular ozone and HO[•], and thus affects ozone decomposition. In past studies, Hoigne and Bader (1978) concluded that ozone does not oxidize ammonium (NH₄⁺) due to the lack of electrons. Also radiolytic and gas-phase studies indicate that HO[•] can only oxidize NH₃, but not NH₄⁺ (Rigg et al., 1952; Lati and Meyerstein, 1972). However, when compared against other constituents existing in natural waters, the reaction of ammonia with ozone is slow and the rate is usually less than some major chemical constituents such as NOM and bromine species (see Table 6.3). In addition, the reaction of ammonia as scavenging HO[•] is at least one order of magnitude less compare against other constituents. As a result, the reactions of ammonia with ozone as well as HO[•] in natural waters usually do not have strong impact on ozone decomposition. This is especially true when ammonia concentration is at trace levels, e.g. µg/L.

When ammonia is applied during ozonation for bromate control, the added ammonia dose is based upon the existing bromide levels in waters. Since the average bromide level in the CRW water is below 100 µg/L (1.25 µM), only less than 0.3 mg-N/L (21 µM) of ammonia, in which based upon the molar ratio

of $\text{NH}_4^+/\text{Br}^- = 15$, is needed to achieve maximum reduction of bromate. The addition of such low amount of ammonia to minimize bromate formation will not affect ozone decomposition as well as HO^\bullet scavenging and thus the R_{CT} remains unchanged. In general, if the added amount of ammonia is less than 0.5 mg-N/L, R_{CT} will not be affected by ammonia while maximum reduction of bromate formation can be achieved even when the level of bromide in water is up to 200 $\mu\text{g}/\text{L}$.

16.5.2. 6.5.2 Competition of Reactions

When intermediate aqueous bromine is formed during ozonation process, this highly reactive species will continue to react with ozone and HO^\bullet to form bromate as the end product. Meanwhile, it can also react with NOM and ammonia, which lead to alter bromate formation pathways. Figure 6.12 shows possible reaction pathway resulting in bromate reduction. Our study (Chapter 7) concluded that reaction rate of bromine with pre-ozonated NOM present in CRW water is on the order of $15 \text{ M}^{-1}\text{s}^{-1}$. Compared to the reaction with ammonia ($7.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$), the rate is several orders of magnitude higher, which means that bromate reduction by ammonia addition is overwhelmingly predominant.

This predominant reaction of ammonia and HOBr is controlled by the concentrations of the respective species. The speciation of these compounds is dependent on water pH. Based on rate calculation considering species distribution at different pH ranges, Figure 6.13 shows that the maximum rate of $[\text{NH}_3]$ reaction with $[\text{HOBr}]$ is achieved at pH 9.05 ($1/2 * (\text{pK}_{\text{HOBr}} + \text{pK}_{\text{NH}_4^+})$) and declines with increasing pH. Figure 6.14 shows that for typical waters, within the pH range of 6.5 to 9, the formation rate of monobromamine is favored with increasing pH and $\text{NH}_4^+/\text{Br}^-$ molar ratio, and thus bromate reduction is enhanced. Furthermore, high ammonia concentration prevents ammonia from rapidly depleting by the cyclic $\text{OBr}^- \rightarrow \text{NH}_2\text{Br} \rightarrow \text{Br}^-$ reactions during ozonation and thus minimizes reoccurrence of bromate formation by direct and direct/indirect pathways.

16.5.3. 6.5.3 Change of Bromate Formation Pathways

Contribution of bromate formation from the three major possible pathways varies with changing pH as well as the addition of ammonia. At water pH 6.5 where bromine species is predominant by HOBr ($[\text{OBr}^-]/[\text{HOBr}] = 5.0 \times 10^{-3}$), bromate formation is mainly contributed by HO^\bullet oxidation pathways (e.g.,

I/D pathways). As pH increases by one unit to 7.5, bromate formation increases exponentially due to higher portion of OBr^- (e.g., 10 times higher than at pH 6.5) and more HO^\bullet exposure despite, in the meantime, ozone exposure slightly decreases. When pH increases to 8.5, OBr^- species rapidly increases and thus formation of bromate becomes predominated by D and D/I pathways via intermediate OBr^- (see Figures 6.6-6.8). This observation can be indirectly proved by later ammonia addition experiments. When ammonia is added into water, the contribution of bromate formation by D and D/I pathways are blocked (Hofmann and Andrews, 2001) and thus bromate formation shifts to the I/D pathway. The degree of decreasing contribution of bromate formation by D and D/I pathways is dependent upon the amount of (added) ammonia. Maximum reduction can be achieved as OBr^- is totally blocked by ammonia. On the other hand, the efficiency of bromate reduction by ammonia is increased with increasing the concentration and is enhanced as water pH increases. Figures 6.6-6.8 show that when excess of ammonia was added ($\text{NH}_4^+/\text{Br}^-$ molar ratio >15 , on the basis of Br^- concentration), maximum bromate reduction efficiency was achieved by 10%, 60%, and 85% at 20 minutes at pH 6.5, 7.5 and 8.5, respectively. However, bromate formation can not be totally reduced by ammonia since HO^\bullet oxidation pathways have minimal effect on the reactions with ammonia and thus can continue to gradually form bromate. Figures 6.6 to 6.8 demonstrated that even very high dose of ammonia was applied, some small amount of bromate still formed.

16.5.4. 6.5.4 Limitations of Ammonia on Bromate Formation

Ammonia addition cannot totally reduce bromate formation due to its inability to inhibit the indirect bromate formation pathways. Therefore, if waters contain high bromide level, using ammonia to control bromate below MCL is probably impractical unless further bromate reduction and/or removal treatment is applied. In addition, the presence of ammonia only delays the formation of bromate. Once ammonia is depleted in the cyclic $\text{OBr}^- \rightarrow \text{NH}_2\text{Br} \rightarrow \text{Br}^-$ reactions to form bromamines and nitrate, bromate formation resumes. Rates of these cyclic reactions increase with increasing ozone exposures and higher ammonia concentrations. In general, the curves of nitrate formation

over time are similar to bromate formation curves during ozonation (Figure 6.15). Furthermore, since the extent of adding ammonia to minimize bromate is dependent on water pH, the pH level of the water should be taken into account when designing ammonia control strategies.

16.6. 6.6 CONCLUSION

Effects of ammonia on bromate mitigation as well as on ozone disinfection (e.g., ozone exposure and HO[•]) during ozonation are summarized below:

- Ammonia can effectively reduces bromate formation in ozonated waters containing bromide ion and the reduction efficiency is enhanced at higher water pH.
- Compared to the raw CRW water that has no detected ammonia, it is observed that little effect on bromate reduction at pH 6.5 and less than 10% of bromate reduction at 20 minutes even when high dose of ammonia is applied.
- Up to 60% and 85% of bromate reduction were achieved at pH 7.5 and 8.5, respectively when the molar ratio of NH₄⁺/Br⁻ is greater than 15. However, beyond this maximum point, even a very high dose of ammonia is applied some bromate still formed and additional reduction is due to consumption of ozone by ammonia, which results in less ozone residuals remaining in waters.
- Addition of ammonia does not affect ozone decomposition due to its slow reaction with both ozone and HO[•], and therefore, R_{CT} remains unchanged. Based upon bromate formation pathways, intermediate aqueous bromine can be inhibited by reacting with ammonia to prevent further oxidation via both direct/indirect and direct pathways. It can be concluded that ammonia addition for controlling bromate formation does not alter the [HO[•]]/[O₃] ratio, but shifts bromate formation towards the HO[•] oxidation pathway by scavenging HOBr/OBr⁻.
- Based upon the bromide level in the water, maximum bromate mitigation can be achieved when the molar ratio of NH₄⁺/Br⁻ is stoichiometrically greater than 15.
- Ammonia cannot totally reduce bromate formation because reactions through the radical pathways also contribute a significant amount of bromate. Bromate mitigation by ammonia addition is not

efficient in waters with low pH and/or already containing high ammonia levels. This observation is important in practical application when considering bromate control using ammonia in water treatment facilities. The addition of ammonia probably cannot achieve bromate mitigation to below the MCL if waters contain greater than 0.5 mg/L of high bromide levels.

16.7. REFERENCES

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Table 6.1- Values of R_{CT} in batch ozonation experiments at various pH and ammonia dosages (condition: O_3 : 3 mg/L, Br^- : 2.1 μ M, temperature: 24 °C).

NH_4^+/Br^-	$R_{CT}/10^{-9}$ (0-2 minutes)	$R_{CT}/10^{-9}$ (2-20 minutes)
pH 6.5	0-15	7.5±1.1
pH 7.5		18 ±1.7
pH 8.5		30 ±3.0
		16 ±1.7

Table 6.2- Values of R_{CT} in continuous flow ozonation experiments at various pH and ammonia dosages (condition: Br^- : 70 μ g/L, pH 8.2, temperature: 24 °C).

NH_4^+/Br^-	$R_{CT}/10^{-9}$ (slow stage)
0	25.7
1	25.2
3	25.0
10	27.5

Table 6.3- Rate constants of chemical reactions with ozone and HO[•].

Compound (i)	$k_{O_3,i} (M^{-1}s^{-1})$	Reference	$K_{HO\bullet,i} (M^{-1}s^{-1})$	Reference
Br ⁻	160	Hoigne and Bader, 1983 III	5.0×10^9	Buxton, 1968
BrO ⁻	100	Hoigne and Bader, 1983 III	4.2×10^9	Buxton, 1968
Cl ⁻	<0.003	Hoigne and Bader, 1983 III	4.2×10^9	Buxton, 1968
CO ₃ ²⁻	<1	Hoigne and Bader, 1983 III	4.0×10^8	Buxton, 1968
NH ₃	20	Hoigne and Bader, 1983 II	1.7×10^7	Meyerstein, 1972
NOM	$\sim 10^4$	Legube et al., 1993; Westerhoff, 1995	4.8×10^8	Kim et al., 2000
OH ⁻	70	Hoigne and Bader, 1983 III	---	
PCBA	0.15	Yao and Haag, 1991	5.0×10^9	Haag, and Hoigne, 1981

Table 6.4- Competition kinetics for aqueous bromine (conditions: O₃ dose: 3 mg/L; HOBr/OBr⁻ = 2.1 μM, NH₃=32 μM, pH 8.5)

Species	Conc. (Ci)	$k_{HOBr,i} Ci (s^{-1})$	$k_{OBr,i} Ci (s^{-1})$	Fraction _{(HOBr/OBr⁻), i}
NH ₃	3.20×10^{-5}	7.5×10^7	<1	>99.99
O ₃	6.25×10^{-5}	<0.01	100	<0.01
HO [•]	1.87×10^{-12}	2.0×10^9	4.2×10^9	<0.01

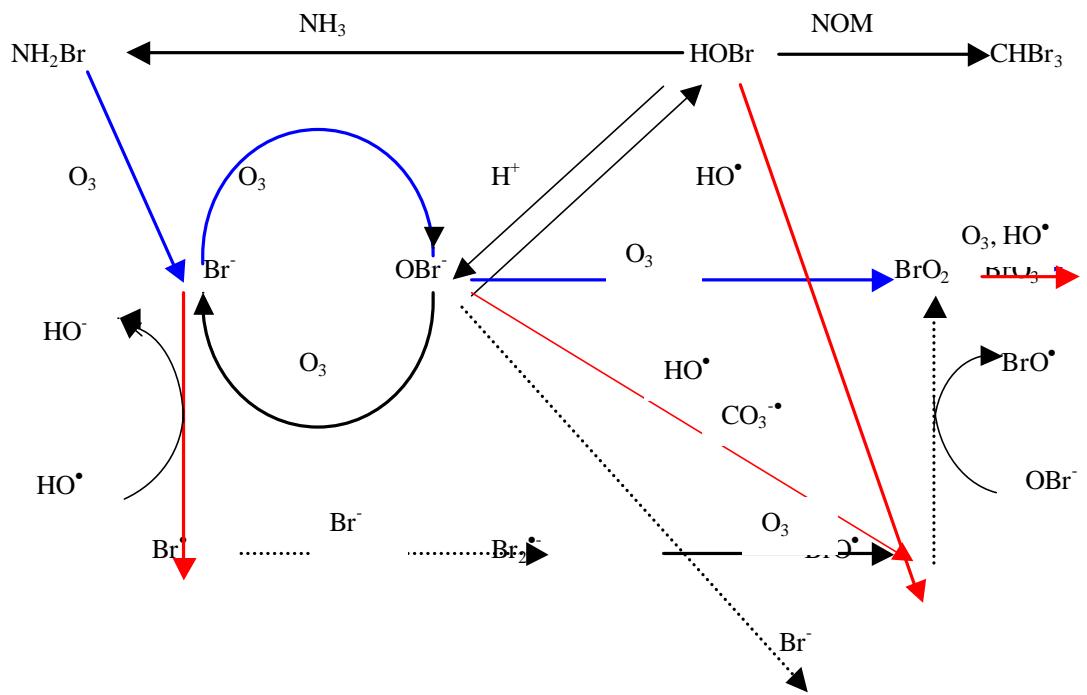


Figure 6.1 - Schematic representation of bromate formation by molecular ozone and hydroxyl radicals (blue solid lines represent ozone reaction pathways; red solid lines represent HO^\bullet reaction pathways, black dashed lines represent radical bromine transformation).

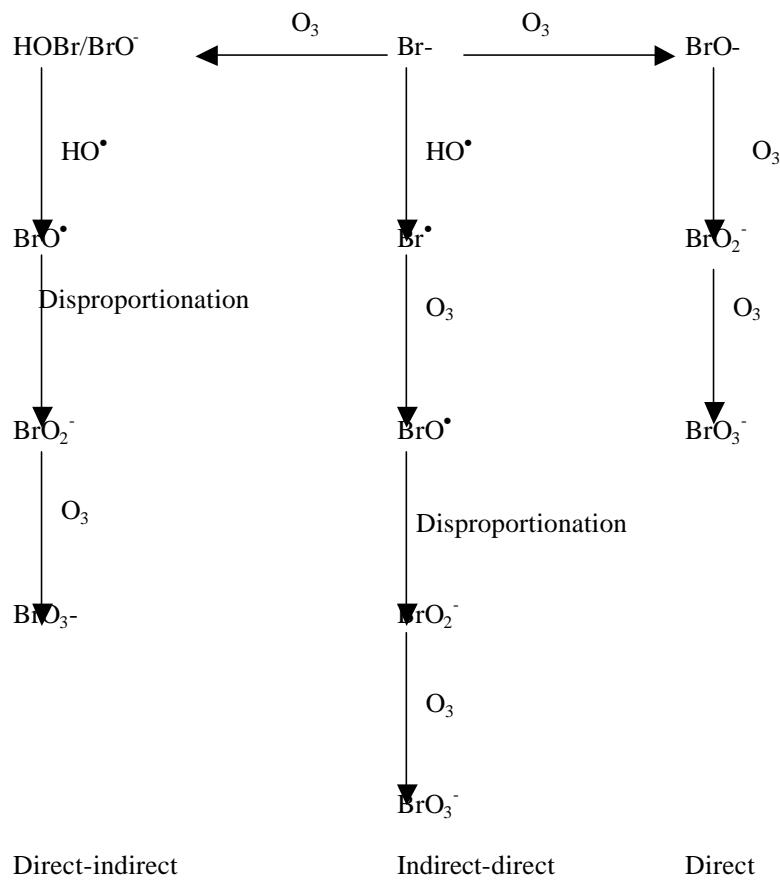
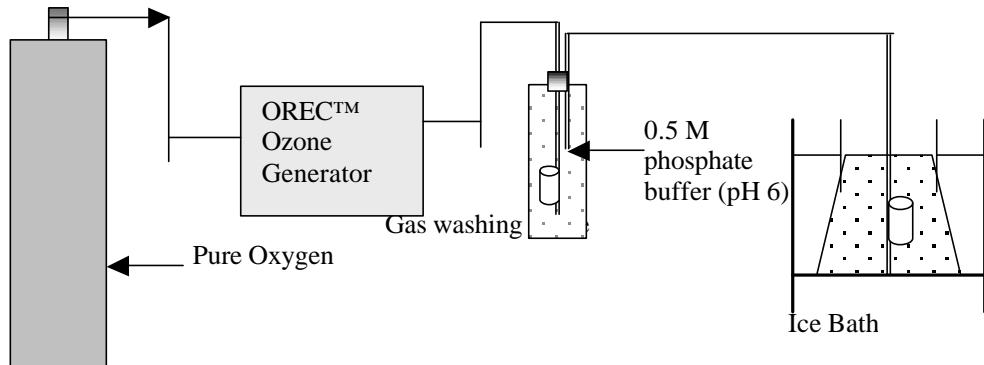
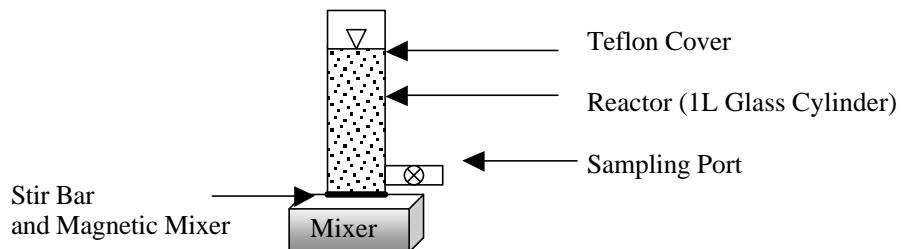


Figure 6.2- Three major bromate formation pathways.



(a) Stock ozone generator.



(b) Batch ozonation reactor.

Figure 6.3- Schematic layout of (a) stock ozonation generation system and (b) batch ozonation reactor.

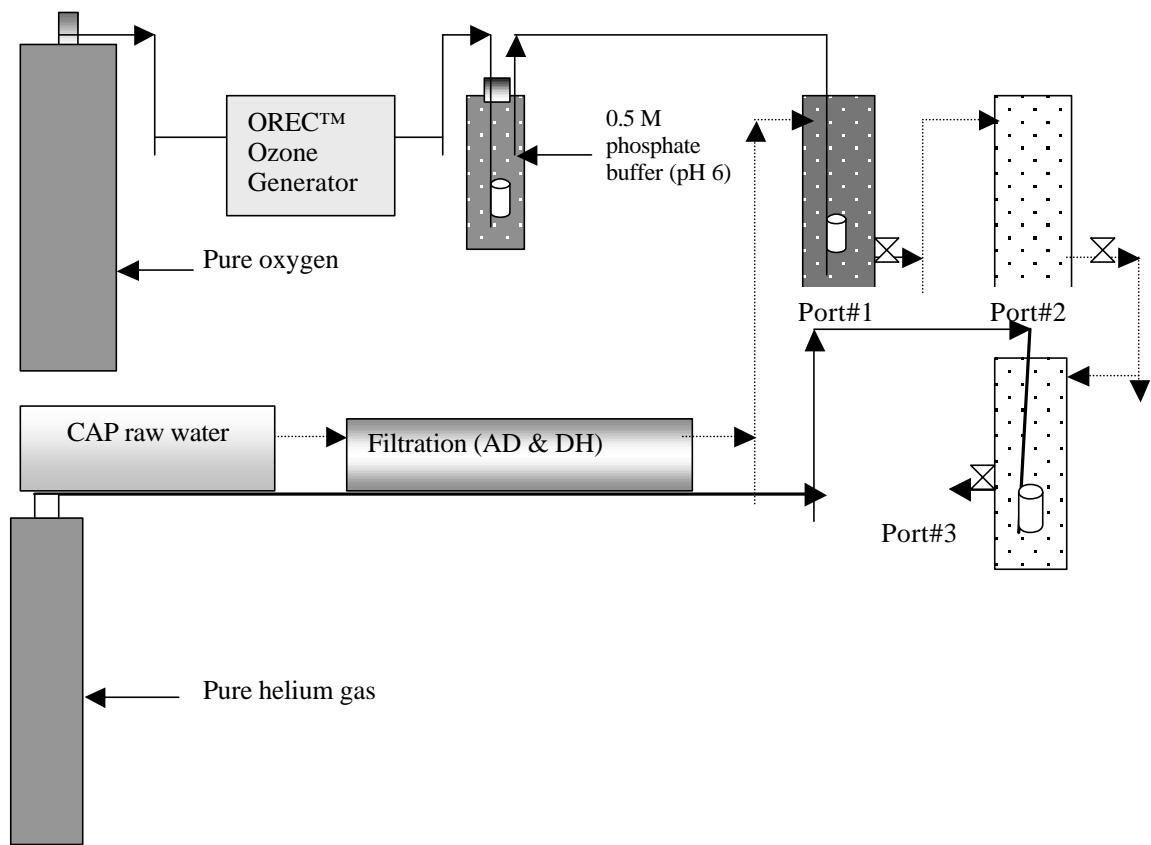


Figure 6.4- Schematic layout of continuous flow ozonation unit (dashed arrows represent water flows during continuous flow ozonation experiments).

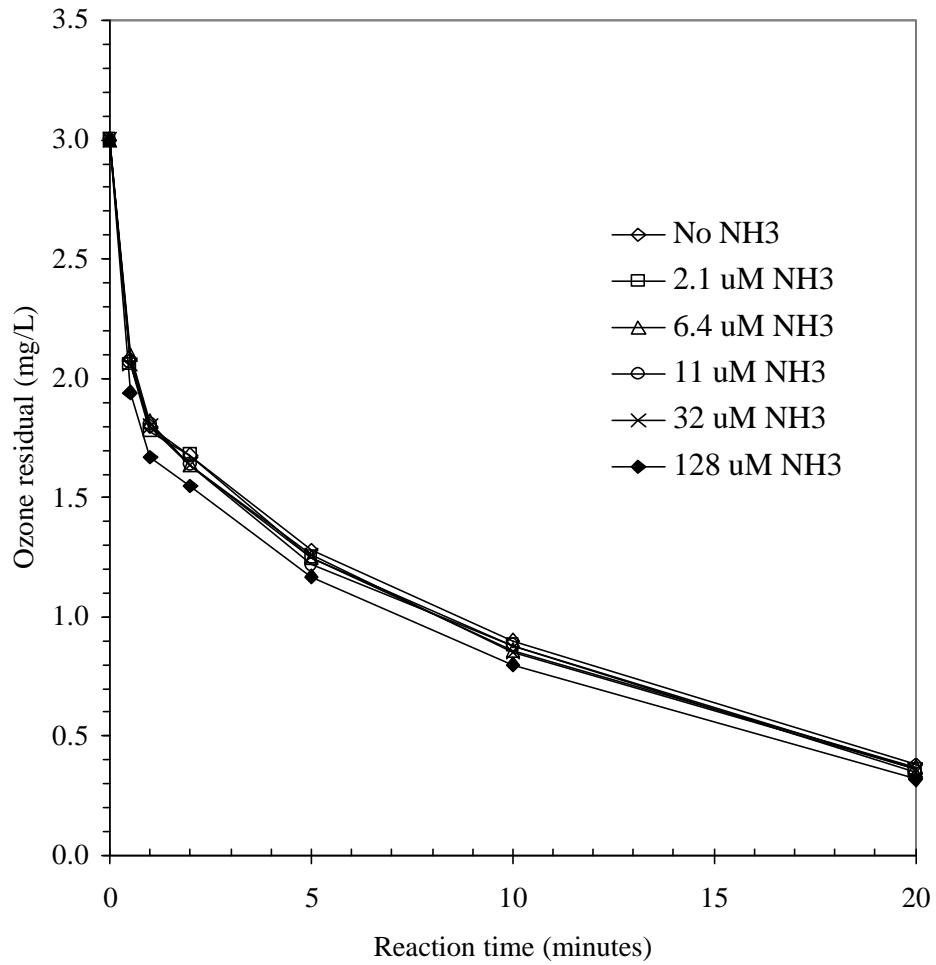


Figure 6.5- Effect of ammonia on ozone decomposition in batch ozonation experiments (conditions: O₃: 3 mg/L; temperature: 24 °C; pH 7.5; bromide: 2.1 μM).

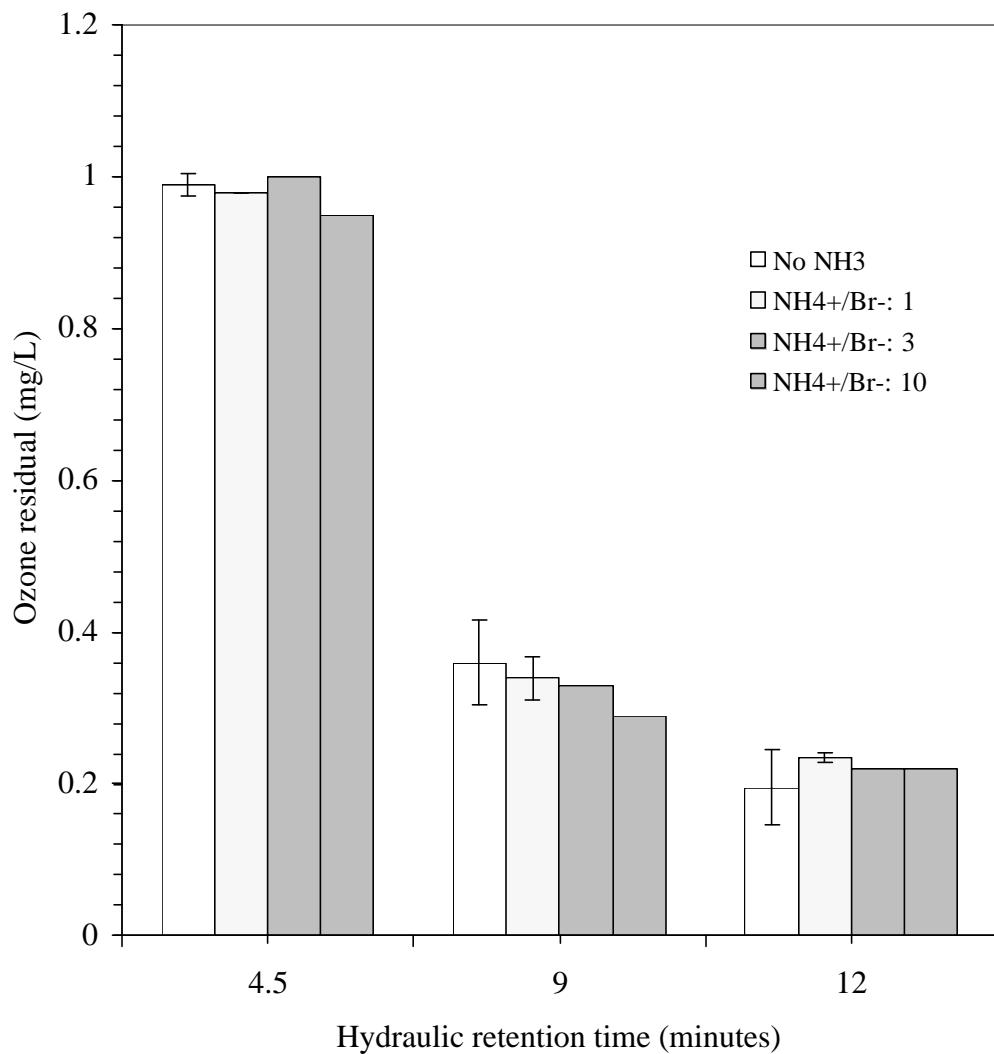


Figure 6.6- Effect of ammonia on ozone decomposition in continuous flow ozonation experiments (conditions: temperature: 24 °C; pH 8.2; bromide: 0.9 µM).

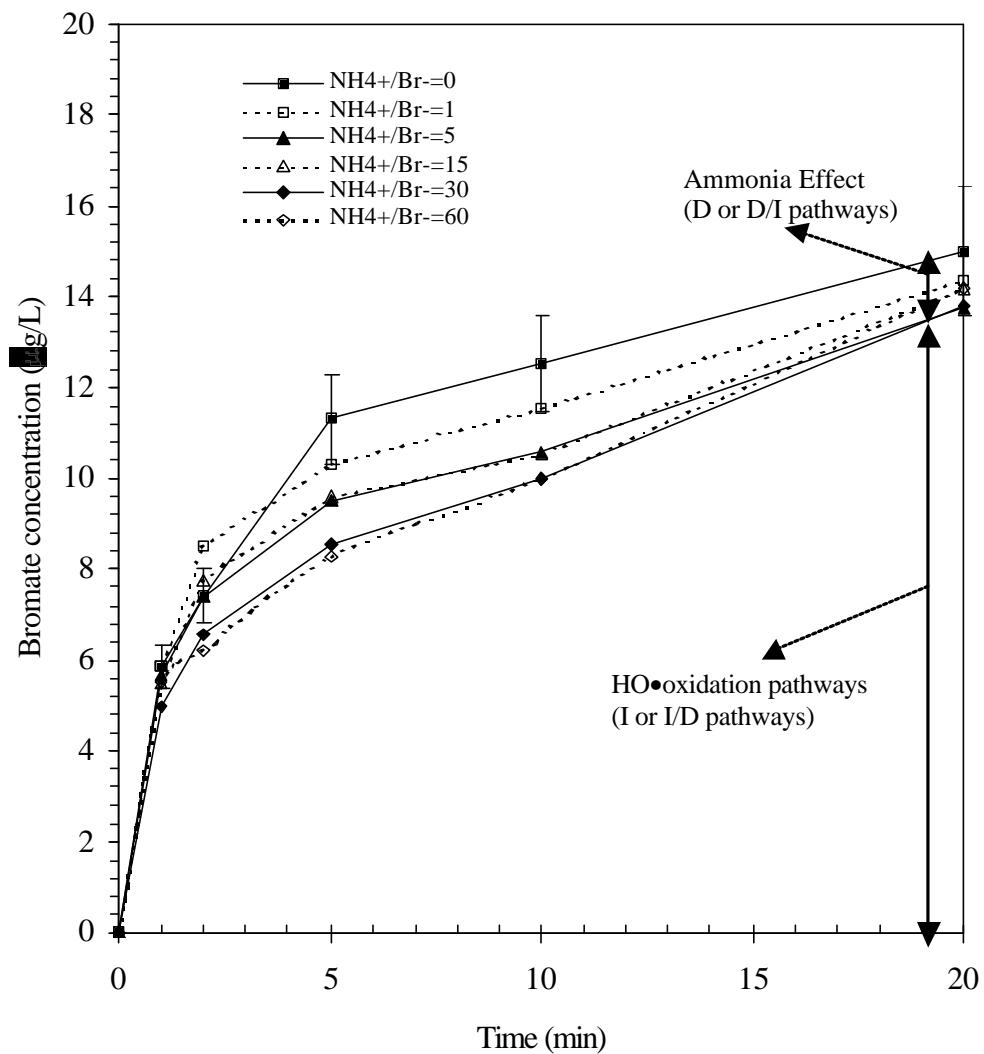


Figure 6.7- Effect of ammonia (in molar ratios) on bromate formation in batch ozonation experiments at pH 6.5 (conditions: O_3 : 3 mg/L; temperature: 24 °C; bromide: 2.1 μM).

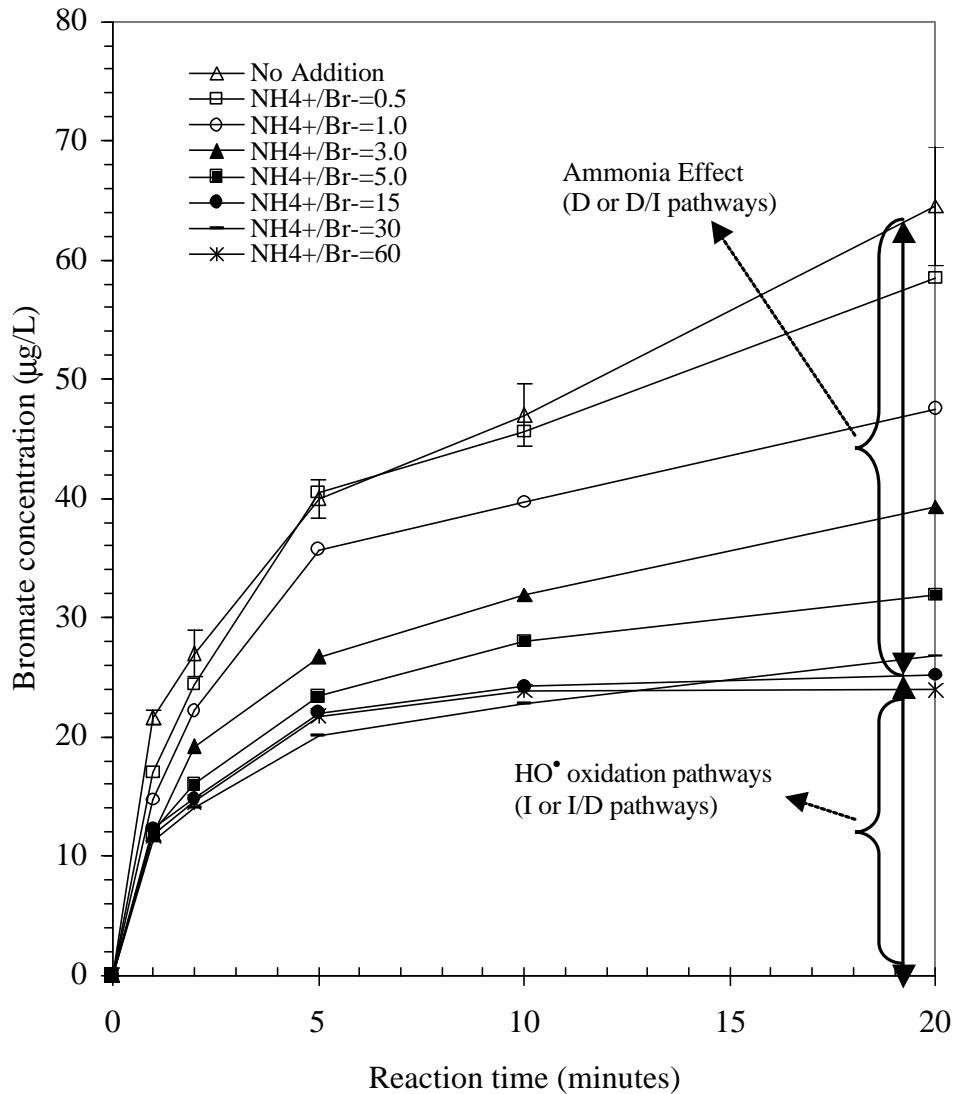


Figure 6.8- Effect of ammonia on bromate formation in batch ozonation experiments at pH 7.5 (conditions: O_3 : 3 mg/L; temperature: 24 °C; bromide: 2.1 μM).

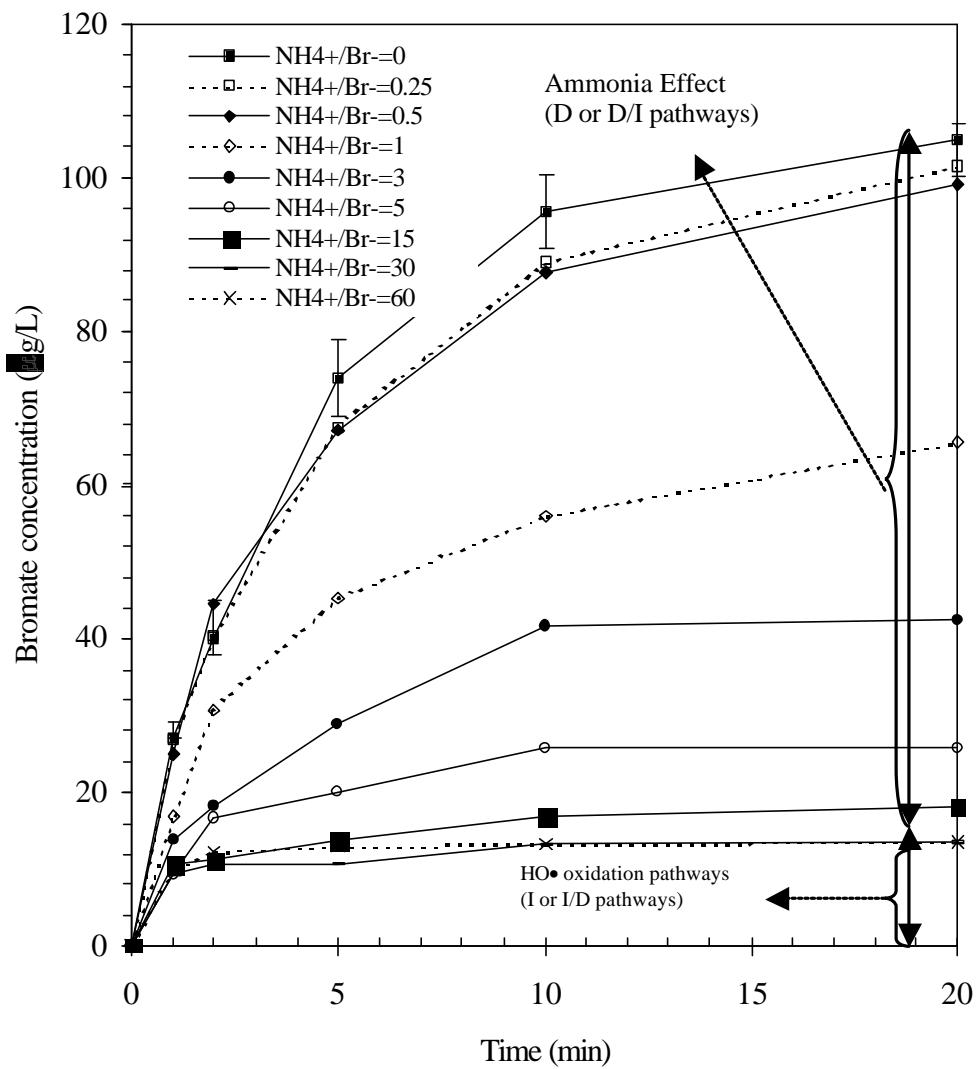


Figure 6.9- Effect of ammonia dosage on bromate formation in batch ozonation experiments at pH 8.5 (conditions: O_3 : 3 mg/L; temperature: 24 °C; bromide: 2.1 μM).

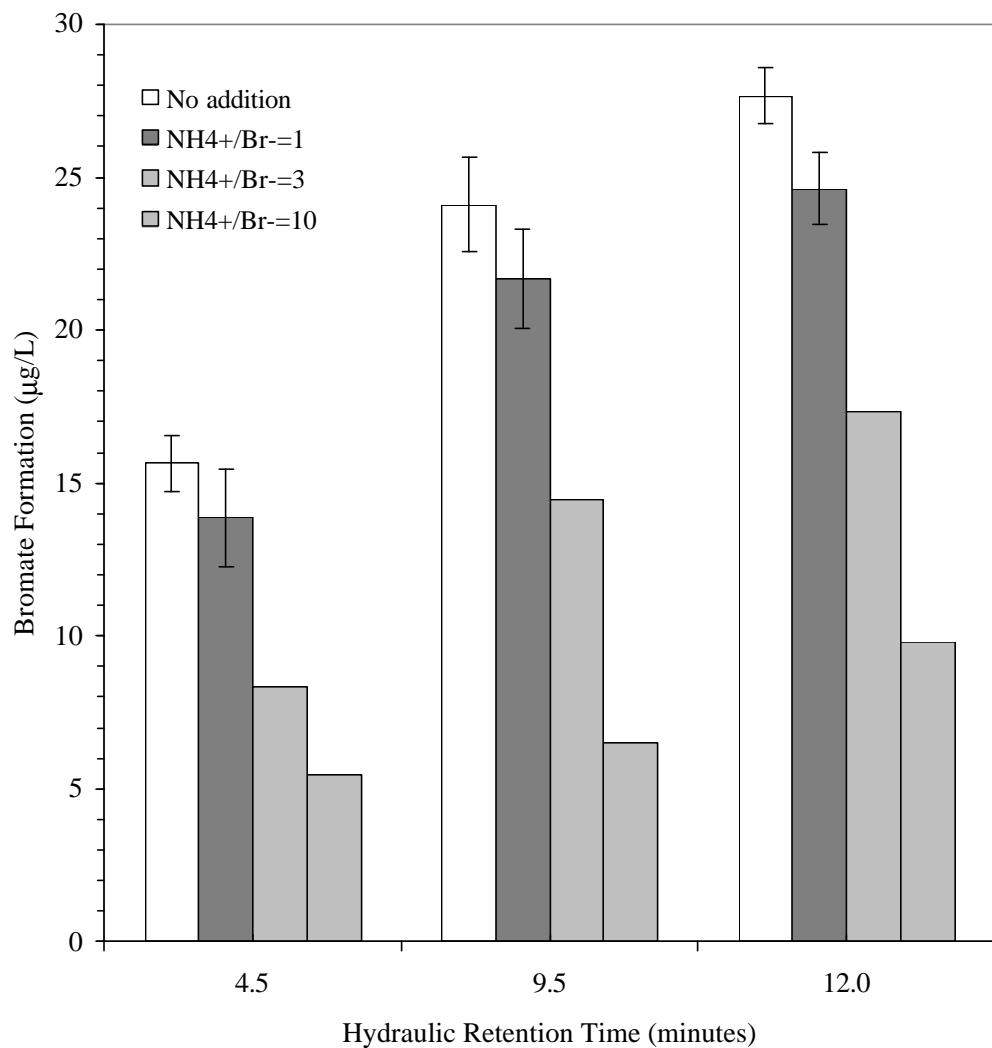


Figure 6.10- Effect of ammonia on bromate formation in continuous flow ozonation experiments (conditions: temperature: 24 °C; pH 8.2; bromide: 0.9 µM).

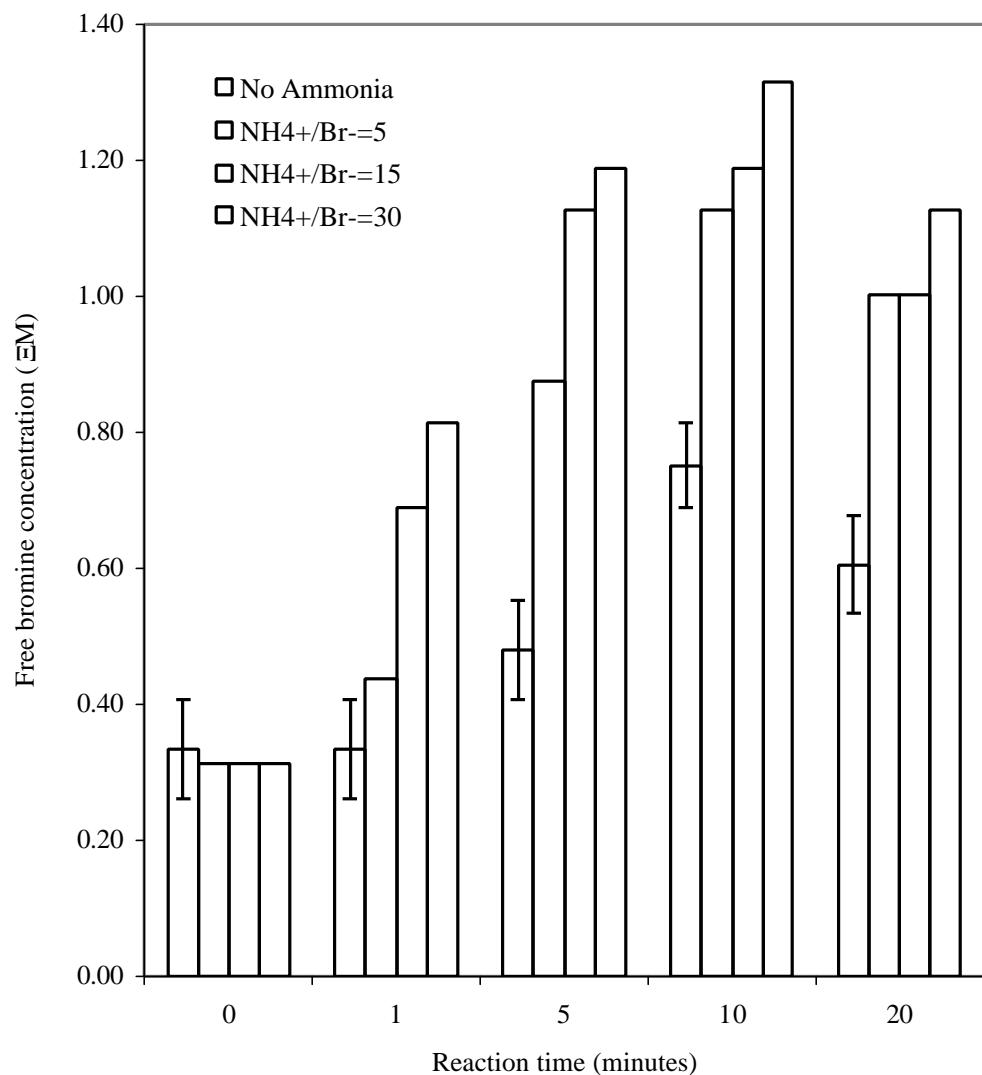


Figure 6.11- Intermediate aqueous bromine formation in batch ozonation experiments (conditions: O₃: 3 mg/L; temperature: 24 °C; pH 7.5; bromide: 2.1 μM).

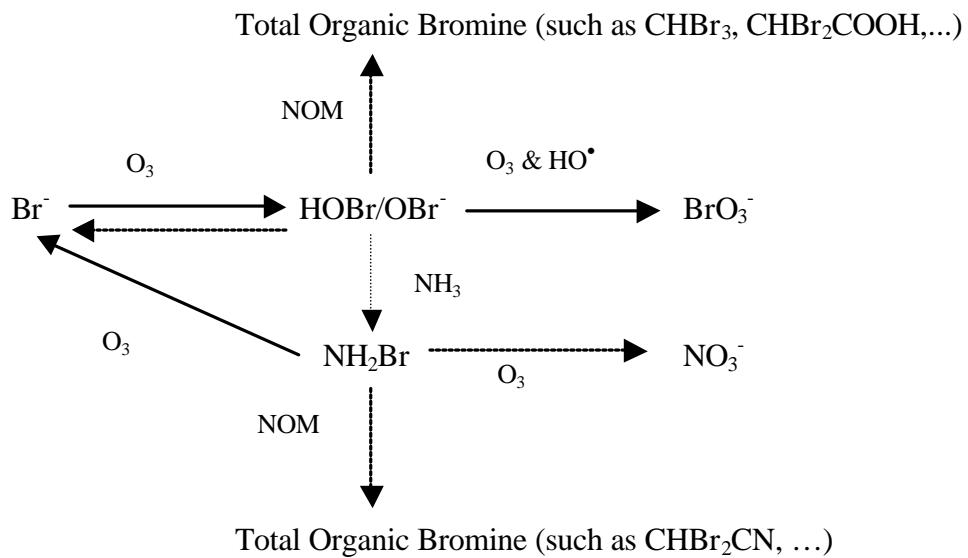


Figure 6.12- Possible reaction pathways of bromine species during ozonation process
(solid lines represents favorable of bromate formation and dashed lines represent unfavorable of bromate formation).

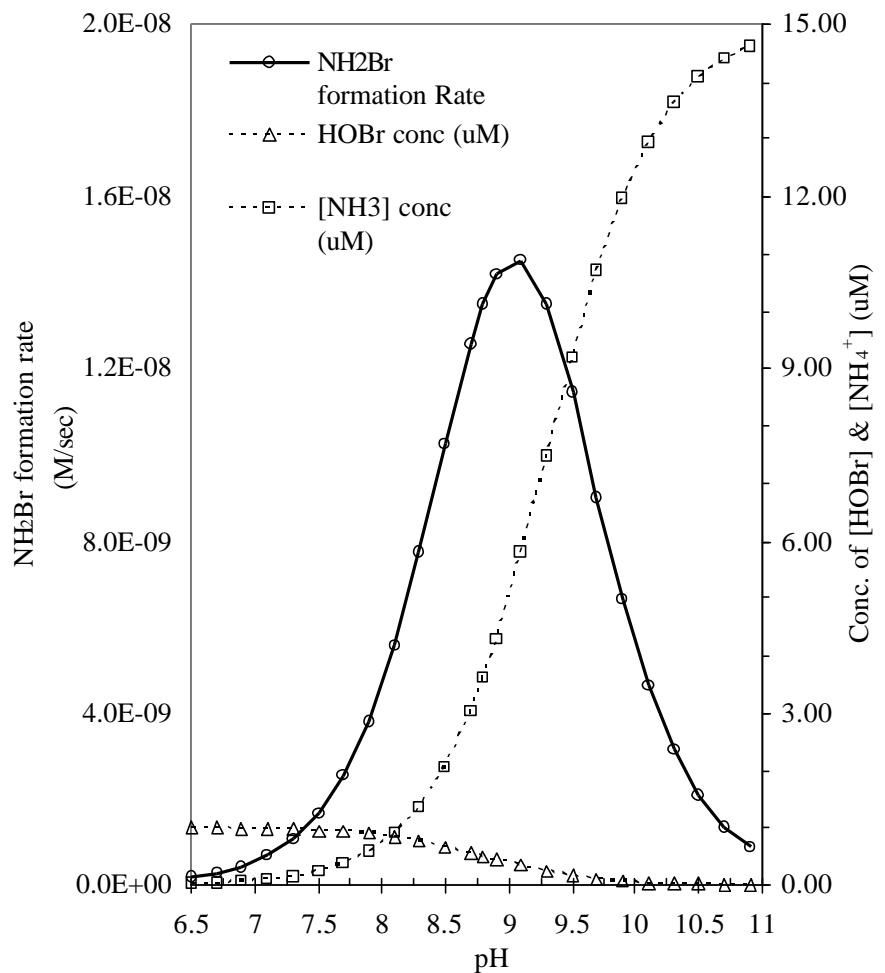


Figure 6.13- Rate calculation of monobromamine formation (conditions:
 $[\text{NH}_4^+]/[\text{HOBr}]_{\text{Tot}} = 15$)

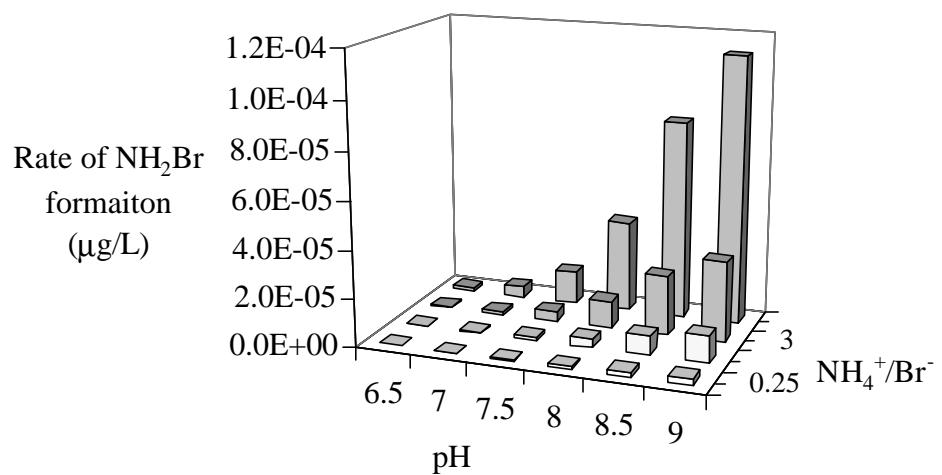


Figure 6.14- Kinetic simulation for reaction rate of monobroamine (Br⁻ or HOBr: 1 μM).

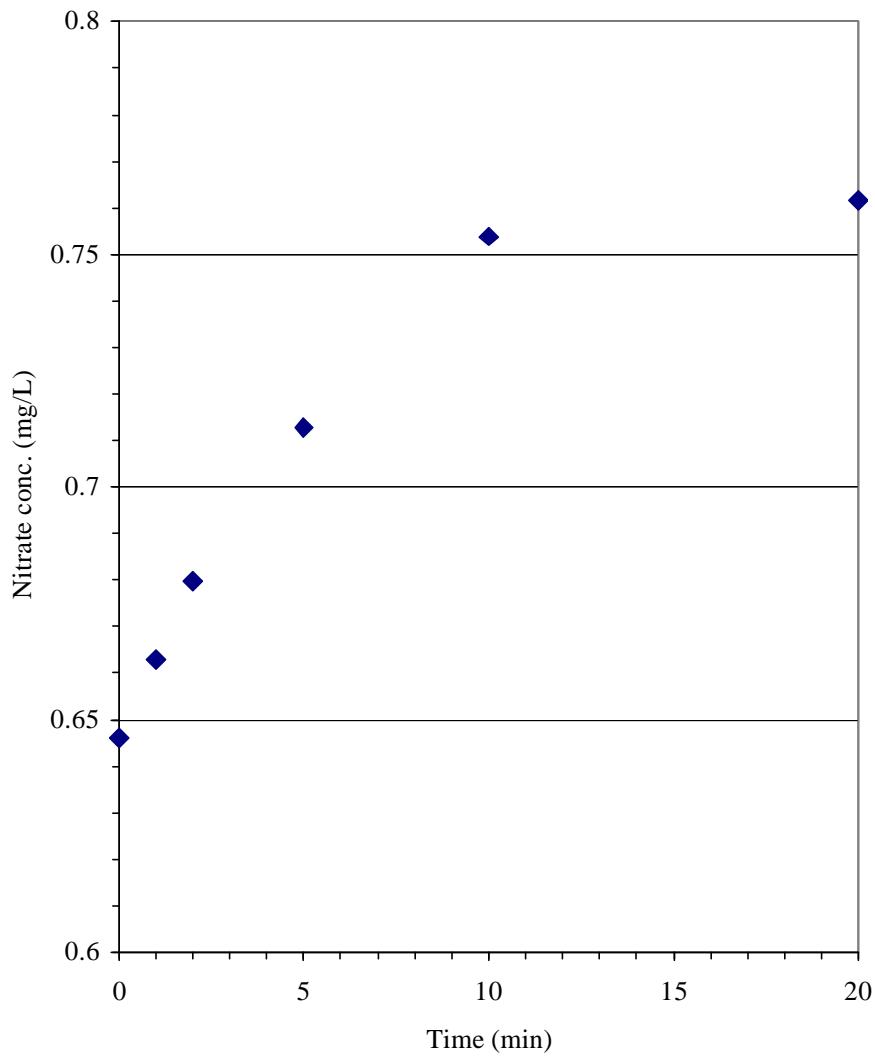


Figure 6.15- Nitrate formation during kinetic batch ozonation (ambient NO_3^- : 0.64 mg/L; Br^- : 170 $\mu\text{g}/\text{L}$, molar ratio of ammonia: $\text{NH}_4^+/\text{Br}^-$: 3; ozone dose: 3 mg/L).

17. CHAPTER 7

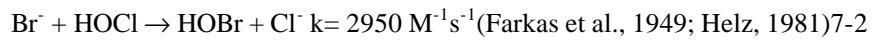
18. REACTIVITY AND DISINFECTION BY-PRODUCT FORMATION OF AQUEOUS CHLORINE AND BROMINE WITH NATURAL ORGANIC MATTER

18.1. 7.1 INTRODUCTION

Disinfection by-products (DBPs) can be formed during oxidation/disinfection of waters containing natural organic matter (NOM) and bromide ions (Br^-), which both exist ubiquitously in drinking water sources (Minear and Amy, 1996). Halogenated trihalomethanes (THMs) and haloacetic acids (HAAs) are the two major classes of DBPs commonly found in waters disinfected with chlorine, whereas bromate ions (BrO_3^-), an inorganic DBP, form during ozonation. Many DBPs in drinking water are suspected to be toxic, carcinogenic, and mutagenic to humans if ingested over extended periods of time (Smith et al., 1992; Glaze et al., 1993; Minear and Amy, 1996). In general, brominated organic species are more carcinogenic among those DBPs in test animals (Bull and Kopler, 1991). Thus, in order to reduce the public health risk from these toxic compounds, the United States Environmental Protection Agency (USEPA) has regulated in Stage I of the disinfection/disinfection by-products rule (D/DBP Rule) the maximum contaminant level (MCL) of THMs, HAAs and BrO_3^- at 80 $\mu\text{g/L}$, 60 $\mu\text{g/L}$ and 10 $\mu\text{g/L}$, respectively. Future regulations could reduce these MCLs to lower levels since the cancer risk levels are higher than the normal regulatory level of 10^{-6} .

NOM reactions with halogens (e.g., aqueous chlorine, bromine, and iodine) have been reported to react via oxidation (i.e., cleaving carbon-carbon double bonds) and/or substitution (i.e., replacement of functional groups by a halogen molecule). Application of aqueous chlorine, e.g., sum of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-),

as a disinfectant will produce organo-chlorine compounds (e.g., chloroform, trichloroacetic acid, etc). When waters contain bromide ions, they can be easily oxidized by ozone or by aqueous chlorine and form aqueous free bromine as intermediates that hydrolyze into hypobromous acid (HOBr) and hypobromite ions (OBr^-) prior to forming DBPs such as inorganic bromate and/or organo-bromine compounds. Rate constants between Br^- with HOCl are higher than with O_3 based upon the reported values from the following reactions:



During the ozonation process, highly reactive HOBr/OBr^- formed from oxidation of bromide may react with NOM, while a portion is further oxidized by ozone and/or hydroxyl radicals to ultimately form bromate. This brings a question that whether the reaction between HOBr/OBr^- and NOM is fast enough to affect bromate formation during ozonation. On the other hand, during the chlorination process HOBr/OBr^- , as well as HOCl/OCl^- , will react with NOM to form organo- bromine and chlorine by-products. It has been observed that organo-bromine compounds (e.g., CHBr_3) are formed more rapidly than organo-chlorine compounds (e.g., CHCl_3) during chlorination. Another unresolved question is whether HOBr/OBr^- serves as a more efficient substituting halogen than HOCl/OCl^- , or does HOBr/OBr^- only react more rapidly with NOM than HOCl/OCl^- . It is hypothesized (*Hypothesis IV*) that “*Aqueous bromine has a higher rate constant with NOM than aqueous chlorine. The rate of reaction between bromine and chlorine with NOM is affected by the characteristics of NOM and pH*”.

NOM in natural waters consists of a heterogeneous mixture of humic substances, hydrophilic acids, protein, lipids, carbohydrates, carboxylic acid, amino acid, and hydrocarbons (Thurman, 1985; Hayes et al., 1989). NOM is considered the primary organic precursor to DBP formation and is generally quantified using a surrogate parameter such as total organic carbon (TOC) or dissolved organic carbon (DOC). A recent study by Larson and Weber (1994) suggested that, among organic compounds, m-dihydroxybenzene structures are responsible for DBP formation of chlorination. Because these different components of NOM may exhibit different reactivity with oxidants, knowledge of the reactivity of these NOM components with aqueous chlorine and bromine is central to understanding how to control DBPs in water treatment processes.

Early kinetic studies of the chlorination of phenol and chlorine-substituted phenols by Soper and Smith (1926) and later by Lee (1967) have shown that the overall reaction is second-order and proportional to the concentration of aqueous chlorine and phenol at pH values greater than 6. It is anticipated that NOM reactivity towards aqueous bromine and/or chlorine is ultimately dependant on its characteristics. However, unlike a single organic compound, which has specific physical and chemical properties, the characteristics of NOM from source waters are heterogeneous. Ultraviolet absorbance in the range of 250 to 280 nm ($UV_{254-280}$) and ^{13}C -NMR have been used commonly to characterize NOM (Rostad et al., 2000; Reckhow et al., 1990). In addition, specific ultraviolet absorbance at wavelength 254 nm ($SUVA=UV_{254}/DOC$), a surrogate for aromatic carbon, has often been correlated with DBP formation (Edzwald et al., 1985; Reckhow et al., 1990; Larson and Weber, 1994; Najm et al., 1994; Korshin et al., 1997; Croue et al., 1999). Reckhow et al. (1990) conducted chlorine oxidation studies with several purified hydrophobic organic acids of NOM from several different sources and

found out a significant correlation between aromatic, phenolic, and activated aromatic properties of the NOM fraction and chlorine demand. By following the same basic principles for the reactivity of chlorine with NOM, Symons et al. (1993) found that bromine reacts with organic matter faster and more effectively than does chlorine.

Most of the literature available on the formation mechanisms of halogenated compounds was developed by adding chlorine to waters in the presence of Br⁻. Further investigation on the respective reactivity of NOM with aqueous chlorine as well as aqueous bromine is needed to better understand individual reaction mechanisms, and thus provide improved insight into the development of more effective control of DBP formation during drinking water treatment operation. The goal of this study is to provide a more robust mechanistic understanding into the selectivity of bromine versus chlorine as they react with NOM, and to compare their relative efficiencies as oxidants and substituting agents.

18.2. 7.2 MATERIALS AND METHODS

Materials. All reagents and chemicals were analytical grade. The solutions were prepared with water (~18.3 MΩ) made from an ultrapure water system (Nanopure InfinityTM). The aqueous chlorine stock solution was prepared from sodium hypochlorite (FisherTM, 13% active), whereas aqueous bromine stock solution was prepared from pure liquid bromine (Aldrich, 99.9%). Phosphoric acid (H₃PO₄) and sodium hydroxide (NaOH) were used for pH adjustment. Solutions containing NOM were prepared using lyophilized organic material. Two different types of organic material were applied: 1) a reverse osmosis isolated sample from Swannee River (SR-RO) obtained from the International Humic Substance Society (IHSS) and 2) an isolate concentrated by

nanofiltration, hydrogen saturation, and lyophilization (CRW-NF) obtained from the Colorado River water (CRW) collected from the Central Arizona Project canal near Scottsdale, AZ. Figure 7.1 depicts nanofiltration and XAD-4 resin separation processes. Approximately 2 grams of lyophilized CRW-NF isolate was extracted from 400 L of CRW water. Some stock solutions (3.2 mg/L as C) of organic materials were pre-ozonated using pure gaseous ozone that was generated from pure oxygen (99.999%) by an OREC™ (Model V5-0, Phoenix, AZ) ozone generator (100% voltage) prior to experiments. Gaseous ozone was introduced into 1 L of stock solutions for 5 minutes and then sparged with pure helium (99.999%) to remove residual ozone.

Experimental approach. Three experimental approaches were undertaken to compare differences in bromine versus chlorine reactions with organic matter. Details for these three approaches are described below:

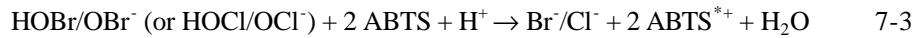
Approach I: Experiments were designed to compare the substitution efficiency of aqueous bromine and chlorine with model organic compounds and NOM. Solutions of model organic chemicals (Table 7.2) were prepared and adjusted to a pH of 7.5 with 1 mM phosphate buffer. Batch halogen experiments with model compounds were conducted in 40mL amber vials with Teflon caps. The halogen dose was selected at 2 mole halogen per mole carbon in the model compounds, thus the conditions would be comparable to those in solutions with NOM where chlorine is dosed based upon a DOC concentration. After 40 minutes of reaction residual halogen concentrations were measured. Simultaneously sodium thiosulfate was added to duplicate vials to quench the halogen residual. Within 24 hours the quenched samples were analyzed for trihalomethanes via methyl-tetra-butanol ether (MTBE) extraction and analysis by gas chromatography.

Approach II: Batch kinetic experiments were conducted to compare the rate of reaction between bromine or chlorine and NOM. Aqueous bromine or chlorine was added separately to solutions containing different sources and concentrations of organic material contained in 500-mL amber glass bottles fitted with a repipetting dispenser. A magnetic stirred was placed in the reactor to provide continuous mixing. While these reactions are typically second-order overall, a pseudo-first-order conceptual approach was applied when DOC concentrations were present in large excess compared to added concentrations of aqueous bromine or chlorine. A 2 μ M concentration of bromine or chlorine was added separately to various initial concentrations of organic materials ranging between 0 to 150 μ M (assuming a carbon molecular weight of 12 g/mole). Changes in residuals of aqueous bromine or chlorine were monitored over time. The pseudo-first rate constants with respect to aqueous bromine and chlorine were calculated and then converted to (second-order) rate constants after experiments at several initial DOC concentrations were performed. Experiments were conducted at a pH value of 5 and at a temperature of 24 °C. Additional experiments at different pH values (pH 8 and 11) and a lower temperature at 10 °C were selected to consider the effects of pH and temperature. In addition, kinetic experiments were conducted to investigate the rate change in pre-ozonated NOM solutions as well.

Approach III: These experiments were designed to compare how bromine or chlorine changed the structure of organic matter. Batch experiments with SR-RO NOM were also conducted at pH 7 to determine changes in ^{13}C -NMR spectra with bromine, chlorine, and without halogen addition. A halogen dose of approximately 5:1 halogen to DOC concentration was used. After reacting for 14 days at 22 °C in the dark, the samples were acidified with HCl to pH 2.2 and sparged with nitrogen to remove residual halogen. Samples were lyophilized and analyzed by solid-state ^{13}C -NMR and ultra/visible (UV/VIS) spectrophotometer.

Analytical methods. Aqueous bromine and chlorine concentrations were measured by the colorimetric N,N Diethyl-P-Phenylenediamine (DPD) method (Standard Method, 1995) using a HACH DR/2000 Spectrophotometer for experiments in approach I and III. In approach II experiments, 2,2-azino-bis (3-ethylbenzothiazoline)-6-sulfonate acid-diammonium salt (ABTS) method (Pinkernell et al., 1997, 2000) was used for measuring residual aqueous chlorine or bromine concentrations. In comparison with the DPD method that is commonly used for measuring aqueous chlorine and bromine, the advantages of using ABTS method over DPD are the much higher stability, faster interaction and lower detection limit (Pinkernell et al., 2000).

Theory behind the ABTS method is that after the samples were withdrawn from the batch reactor and added into prepared ABTS solution, the residuals of chlorine and bromine quickly reacted with excess ABTS and formed ABTS^{*+} via the reaction shown as follow:



The UV Absorbance of ABTS^{*+} measured at wavelength 405nm was then taken for calculation of bromine or chlorine concentration based upon the following equation:

$$[\text{HOBr}/\text{OBr}^- \text{ or HOCl}/\text{OCl}^-] = 0.5[\Delta\text{UVA}_{405\text{nm}}/(\epsilon \times L)] \quad 7-4$$

where $[\text{HOBr}/\text{OBr}^- \text{ or HOCl}/\text{OCl}^-]$ is in mole/L (M); ΔUVA = change of absorbance of sample at 405 nm; $\epsilon = 31,600 \text{ M}^1\text{cm}^{-1}$ at 405nm; L = path length of UV cuvette = 10 cm.

A multi-wavelength UV/VIS spectrophotometer (Shamduz UV-160U) was used to measure the UV absorbance of DOC at wavelength range from 250 to 280 nm and ABTS at 405 nm. DOC concentrations were determined using a Shimadzu TOC 5050A Analyzer (high-temperature catalytic combustion/non-dispersive infrared gas analysis).

Specific UV absorbance (SUVA) was determined by normalizing UVA to DOC concentration (UVA/DOC) (Eaton, 1995). Temperature and pH were measured with a BeckmanTM pH meter that was calibrated with buffers pH 4, 7, and 10 standard solutions before use. THM samples were analyzed using a HP 5890 Series II Gas Chromatograph according to USEPA Method 551.2, with MTBE extraction and NaCl addition. DOC isolates were characterized by solid-state cross polarization-magic angle spinning (CP-MAS) ¹³C-NMR. Employing a 4mm Si4N3 rotor, the samples were spun at 12 kHz and the spectra obtained at 100.58 MHz on a Varian Inova-400 NMR, including a 3 ms contact time and 3 s pulse delay.

18.3. 7.3 RESULTS

18.3.1. 7.3.1 Halogen Consumption and Haloform Production

In comparison with selected model compounds that have similar molecular weight and size, less chlorine and bromine was consumed after 40 minutes in the reaction with maleic acid than with other benzene-substituted compounds (Figure 7.2). Resorcinol, which contains two hydroxyl functional groups (-OH), had the largest halogen (X) consumption. Benzoic acid and analine consumed more chlorine than bromine, while most of the other substituted benzenes consumed similar amounts of bromine and chlorine. Phenol, however, was an exception where higher bromine consumption was observed. Haloform (CHX_3) production, shown in Figure 7.3, was measured in parallel with the halogen consumption experiments for the same 40-minute reaction period. CHX_3 production per mole of organic compound ranged from approximately 0.001 for maleic and benzoic acid to 0.1 for resorcinol. Bromoform (CHBr_3) production upon bromine addition was higher than CHCl_3 production upon chlorine addition for all model compounds except maleic acid and resorcinol

Replication of two experiments resulted in small standard deviations (< 5%) for both halogen consumption and haloform production (not shown). Furthermore, the observed results were consistent with trends reported by Norwood et al. (1980) for a similar database of substituted benzenes (also shown in

Figure 7.2 and 7.3). Overall, these results demonstrated that halogen consumption and yield of haloforms were affected by the degree of aromaticity and the presence of electron donating (hydroxyl, amine) or electron withdrawing (carboxyl) functional groups.

A similar set of experiments were also conducted with CRW aqueous solutions after simulated (jar tests) alum coagulation (25 to 225 mg/L). Simulated alum coagulation removed 5% of the DOC at 25 mg/L of alum and over 40% of the DOC for alum dosages above 150 mg/L. Increasing alum dosages lowered the water pH and decreased both DOC and UV absorbance (data not shown). Filtered aliquots from the jar tests were pH adjusted to 7.5 and then spiked with either bromine or chlorine (0.3 mM) and incubated at 4 °C for 24 hours. Halogen consumption and haloform production are reported in Table 7.3. In all cases for parallel experiments a higher molar concentration of bromoform was produced after bromine addition than chloroform produced after chlorine addition. The halogen substitution efficiency (CHX_3 produced per mole X_2 consumed) was always greater for bromine than chlorine. The bromine substitution efficiency normalized to the chlorine substitution efficiency increased from a factor of 2.5 at 25 mg/L of alum to 5.4, 5.9, and 7.1 at alum dosages of 100, 150, and 200 mg/L, respectively. Thus alum coagulation resulted in organic matrix more susceptible to bromine substitution than to chlorine substitution.

18.3.2. 7.3.2 Aqueous Bromine and Chlorine Reaction Rates with NOM

Kinetic analysis for halogen loss in the presence of NOM had two reaction stages: a rapid initial consumption period followed by a slower consumption period. The cross-over between reactions appears to be approximately 5 minutes for chlorination. However, due to a very rapid initial reaction of bromine with NOM, the rapid stage was selected to begin after the first sample collection ($t < 15$ second). This initial halogen consumption may have been due to halogen reactions with trace inorganics in solution or the glassware, but more likely was associated with highly reactive organic matter sites. The rate of aqueous chlorine or bromine consumption increased with increasing initial

DOC concentration (from 0 to 150 μM). Figure 7.4 illustrates separate kinetic experiments with aqueous chlorine or bromine in the presence of CRW-NF and SR-RO isolates. Aqueous bromine reacted much faster for both isolates (reaction time in seconds) than aqueous chlorine (reaction time in minutes), but the SR-RO isolate appeared to be more reactive toward halogenation.

The rate of the initial rapid consumption phase was greater for the SR-RO isolate than CRW-NF isolate. This indicates that the initial demand is a function of the DOC characteristics where the inorganic matrix is invariant. Due to observed fast reaction rates, rate constants could only be estimated from pseudo-zero order (e.g., change in halogen concentration: Δ bromine $_{15 \text{ seconds}}$ and Δ chlorine $_{5 \text{ minutes}}$) as presented in Tables 7.4 and 7.5. In comparison with chlorine, very rapid reactions between bromine and both NOM isolates resulted in rate constants that are approximately 1-2 orders of magnitude higher than resulting from chlorine. Pre-ozonated NOM isolates decreased the reactivity of halogenation. An observed 30% reduction for bromination and 35% reduction for chlorination occurred in the rapid phase between ozonated sampled for both NOM isolates.

Pseudo-first order rate constants (k') were determined by analysis of kinetic halogen consumption data for the slower consumption period. For example, rate (r) of aqueous bromine reaction with NOM at pH 5 can be expresses as follow:

$$r_{\text{Br}_2(\text{aq})} = k' [\text{Br}_2(\text{aq})]$$

7-5

where $k' = K [\text{NOM}]$ and K is a second order rate constant with units of $\text{M}^{-1}\text{sec}^{-1}$.

Figure 7.5 illustrates linearized plots for the determination of pseudo-first order rate constants for bromine consumption in the presence of the CRW-NF isolate under

different initial DOC concentrations. Bromine or chlorine was also consumed in water without any addition of organic material. This could be due to reaction with trace inorganics in solution or the glassware or existing trace organic contaminants in the pure water where DOC has been detected ($\sim 25 \mu\text{M}$ as C) previously. Second order rate constants K in unit of M^1s^{-1} for halogen consumption relative to the molar concentration of DOC in solution were calculated from the slope of linear regression through k' data plotted as a function of DOC. An example of rate calculation ($30 \text{ M}^1\text{s}^{-1}$) for CRW-NF isolate and SR-RO isolate ($130 \text{ M}^1\text{s}^{-1}$) with aqueous bromine is shown in Figure 7.6.

Table 7.6 lists the second-order rate constants of bromine or chlorine addition to CRW-NF or SR-RO NOM isolates. Parallel experiments (e.g., under conditions of pH 5, 24 °C and DOC: 0-150 μM) showed that SR-RO isolate is more reactive with both halogens than CRW-NF isolate, which approximately was 3-fold for chlorination and 4-fold for bromination. In comparison with reaction rate of aqueous chlorine or bromine with NOM, the second-order rate constant of aqueous bromine reaction with CRW-NF is 18-fold greater than aqueous chlorine with CRW-NF NOM isolate, while aqueous bromine reaction with SRRO is 31-fold greater than aqueous chlorine with SR-RO NOM isolate. Temperature's effect on the reactivity of halogenation was minimal between 10 °C and 24 °C. Experiments examining pH effects showed that the change of pH varied reaction rates for both chlorination and bromination (data not shown). However, only a slight change was observed in the presence of bromine at pH 5, 8, and 11, whereas a 2-fold change was observed with chlorine addition. Highest rate constants occurred at pH 8, whereas increasing or decreasing pH reduced the overall reaction rates. Prorogating SR-RO and CRW-NF NOM isolates reduced the observed reactivity with both chlorine and bromine. Overall, an approximately 50% reduction of reaction rates were observed

for both chlorination and bromination after pre-ozonation of NOM in the slower consumption period.

18.3.3. 7.3.3 Effects of Bromine and Chlorine on UV/VIS and ^{13}C -NMR spectra

UV absorbance (250 to 280 nm) is an indicator of sp^2 -hybridized carbon (e.g., aromatic carbon). Halogen reactions change the structure of NOM. Figure 7.7 shows differential UV/VIS spectra representing the subtraction of spectra relative to the untreated SR-RO spectra after chlorine or bromine addition. The inset of Figure 7.7 shows the UV/VIS spectra for SR-RO isolate (untreated DOC = 1 mg/L) prior to halogen addition. A positive value for the differential spectra across wavelengths from 250 to 500 nm on chlorination as well as bromination indicates a decrease in absorbance at a specific wavelength. Chlorine addition resulted in a larger differential decrease in UV/VIS absorbance than bromine addition. The largest difference in absorbance from the untreated SR-RO spectra occurred at 260 nm with a 48 percent reduction in absorbance upon chlorine addition and only a 7 % decrease upon bromine addition. Similar trends occurred in the change of SUVA, where approximately half of the UV absorbance was reduced in chlorination but only slight reduction in bromination (Table 7.7). In addition, ozonated NOM altered the aromatic NOM structure in which SUVA values were reduced by 38 % and 43 % for CRW-NF and SR-RO, respectively (Table 7.7).

Solid-state ^{13}C -NMR spectra for three different SR-RO isolates (untreated, brominated, and chlorinated) are presented in Figure 7.8. ^{13}C -NMR spectra were duplicated to confirm the observed results. The untreated SR-RO sample, that had been pH adjusted in similar fashions as the brominated and chlorinated samples, had a ^{13}C -NMR spectra typical of a sample dominated by humic and fulvic acid material and was characterized by a relatively large amount of material in the aromatic region (110-160 ppm). Table 7.8 summarizes changes in the percentage of response area within specific shift wavelength

regions of the ^{13}C -NMR spectra that are indicative of certain carbon bonding and functional group arrangements. It was observed that the percentage of aromatic region between 110-160 ppm for CRW-NF isolate is less than SRRO isolate, which supported that NOM of CRW-NF is less reactive than the NOM of SRRO.

Compared against the untreated, chlorinated, and brominated SR-RO isolates, bromine addition resulted in only minor changes in the ^{13}C -NMR spectra (Table 7.8). To further illustrate differences between the spectra, differential ^{13}C -NMR spectra (relative to the untreated SR-RO isolate) are illustrated in Figure 7.8 (lower) where spectra response regions that clearly deviate from background signal to noise can be distinguished. Both chlorine and bromine addition decreased spectra response between 0 and 60 ppm (aliphatic carbon range) and 100 to 160 ppm (aromatic carbon range). A decrease in the anomeric range (90 to 110 ppm) was not distinctively evident. Chlorination also resulted in a decreased spectra response between 190 and 220 ppm (ketones). Spectra responses were unchanged within 60 to 90 ppm range (aliphatic carbon bonded with an oxygen atom) or 160 to 190 ppm (carboxyl carbon) range. In general, chlorination resulted in a much more significant change in the ^{13}C -NMR spectrum of SR-RO than bromination. Since the solid-state ^{13}C -NMR analytical method employed cross polarization to protons, it was possible that a portion of the reduced spectra response was due to halogen substitution into organic matter at sites where protons would have otherwise been located. This may have been a primary factor in the reduced response for the aliphatic carbon region from 0 to 60 ppm since this is the region where primary carbon bound with bromine (20 to 40 ppm) or chlorine (25 to 50 ppm) would be represented. However, bromine and chlorine addition appeared to significantly affect the aromatic carbon region, and in the case of chlorine the ketone region as well.

18.4. 7.4 DISCUSSION

Both aqueous chlorine and bromine are fairly reactive oxidants toward organic compounds. They also can substitute into organic compounds. The redox reactions of aqueous chlorine and bromine in water computed from thermodynamic data are listed below (Lingane, 1958):



HOCl ($E_{\text{red}}^{\circ} = +1.49$ V) is a more powerful oxidizing agent than HOBr ($E_{\text{red}}^{\circ} = +1.33$ V) due to its higher electrode potential. However, in aqueous solution HOCl and OCl⁻ ($\text{pK}_a = 7.6$) (Morris, 1966), as well as HOBr and OBr⁻, ($\text{pK}_a = 8.8$) (Haag and Hoigne, 1983; Westerhoff, 1995) appear and species distribution is dependent upon water pH. Overall oxidation capability of aqueous chlorine or bromine is a function of pH. In addition, the activities of electrophilic (aromatic) substitution to release electrons to stabilize carbocation are more favorable for Br atom due to its higher electron density and less bond strength than Cl atom.

The chlorine and bromine consumption for model compounds varies depending on their characteristics, but generally a stronger electron donating functional group results in an increase in the rate of reaction. Compounds with -HO functional groups have both high halogen consumption and haloform formation, whereas compounds attach with -COOH functional groups have lower halogen consumption and haloform formation. Based upon the comparison of bromoform to chloroform yields, aqueous bromine is a more effective substituting halogen than aqueous chlorine. Kinetic reactions show that the rate of bromine in reaction with NOM is approximately an order of magnitude higher than chlorine in a pH range between 5 and 11. Although kinetic reactions and mechanisms of halogenation are a function of pH due to speciation changes of the halogen and the NOM (e.g. functional group protonation and deprotonation), both

protonated and deprotonatoin forms of NOM species are expected to react with halogen. Increasing pH from 5 to 11 shifted the dominant chlorine species from HOCl to OCl⁻ and the dominant bromine species from HOBr to OBr⁻. Maximum rate of chlorination occurs at pH 8, which agrees with Gallard and von Gunten (2002) and Rebenne et al. (1996) on model compound studies. However, effects of pH on rate of bromination in which mainly in substitution mechanisms are not strongly affected by pH. In addition, results of temperature effects show that there was only minimal change in rate constants between 10 °C and 24 °C. This agrees with a study by Rebenne et al. (1996) that suggested that temperature changes have minimal effect on rapid reaction of resorcinol chlorination.

Both UV absorbance and SUVA show the differences in unshared electron pairs and the presence of multiple bonds in NOM, which mainly results in oxidation of withdrawing electrons. The difference of UV/VIS spectra and ¹³C-NMR analysis indicate that aqueous chlorine has a stronger tendency in oxidizing NOM, whereas aqueous bromine favors substitution into NOM. In addition, ozonation reduces aromatic carbon content, specifically phenolic carbon, and produces material with increased oxygenated functional group content (e.g., anomeric and ketone) (Westerhoff et al., 1999). Therefore, ozone oxidizes NOM and reduces rate reactions of ozonated NOM in both chlorination and bromination.

18.5. 7.5 IMPLICATIONS

Bromo-containing organic compounds produced during chlorination are due to the oxidation of bromide that is present in the waters to form HOBr/OBr⁻, followed by the substitution of bromine and chlorine into precursor organic compounds. Since aqueous bromine reacts with NOM is much faster than aqueous chlorine, the speciation and

concentrations of THM and HAA formation in chlorination processes are mainly dominated by the ratio of bromide to reactive NOM as well as the ratio of bromide to chlorine concentrations. In chlorination of waters containing bromide, typically the molar ratio of applied chlorine and the existing Br^- is approximately on the factor of 10. Therefore, this could be explained that chlorination and bromination are very competitive during chlorination process and the species of THMs and HAAs formation coexist even though the rate of bromination is much faster than chlorination.

Rapid reaction between bromine and NOM shows that bromate formation can be affected in the presence of NOM waters during ozonation. The extent of bromate reduction is dependent on characteristics of NOM. However, ozone oxidizes both bromide and NOM and the reactivity of NOM is reduced over time while accumulating bromine concentration. NOM in waters only contains a limited number of fast reacting groups and the reactivity is significantly reduced after a few minutes of ozonation. Based on the studies by Song et al., (1996) and Westerhoff et al. (1995) that only less than 10% of total organic bromo-species formed within a few second, it can be implied that effect of bromine reaction with NOM can be minimal and can only occur within the rapid phase.

Chlorination produces what appear to be oxygen containing functional groups, which is similar to those produced during ozonation, in which mainly by oxidation mechanism. These may be biodegradable and lead to increased chlorine demand in distribution systems. Further work should try to measure aldehyde production from chlorination. In addition, a stop-flow technique with ABTS analysis suggest that a better method to characterize fast reacting phase of bromine reaction with NOM.

18.6. 7.6 CONCLUSIONS

Rate determination matrix experiments were conducted with the addition of aqueous chlorine or bromine and various concentrations of different types of NOM (both

unaltered and preozonated forms) under various pH and temperature conditions. In addition, UV absorbance, SUVA and ^{13}C -NMR spectra were applied as tools to quantify and identify the change of characteristics and reactivity of NOM in the chlorination or bromination processes. On the basis of results of the study described in this article, the following specific conclusions can be reached:

- An indirect UV Absorbance method using ABTS as an indicator provides a useful tool in conducting kinetic chlorination and bromination experiments.
- Both HOBr and OBr^- (or HOCl and OCl^-) react with NOM, and the effect of pH as well as temperature does not significantly change the net reaction rate constants.
- Halogen consumption and haloform formation are dependent on the characteristics of the NOM (e.g., aromatic content and functional groups).
- HOCl acts as a stronger oxidation agent with NOM than does HOBr, which is substituted more readily.
- Kinetically, rate constants of bromine reaction with NOM are nearly an order of magnitude faster than similar chlorine reactions. Bromine reaction rate constants with NOM are 30 to $130 \text{ M}^{-1}\text{s}^{-1}$, whereas chlorine reaction rate constants are 1 to $5 \text{ M}^{-1}\text{s}^{-1}$.
- Preozonation, acts mainly on oxidation of NOM, has stronger impact on reducing rate constants of chlorination than in bromination with NOM. Approximately 50% of NOM's reactivity can be reduced by preozonation.

18.7. 7.7 ACKNOWLEDGEMENTS

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18.8. REFERENCES

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Table 7.1- Summary of organic carbon sources.

Reference ID	Material
MAc	Maleic acid ($\text{HO}_2\text{C}(\text{CH})_2\text{CO}_2\text{H}$)
id	
C6-OH	Phenol ($\text{C}_6\text{H}_5\text{OH}$)
C6-NH ₂	Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)
C6-COOH	Benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$)
C6-RES	Resorcinol ($\text{C}_6\text{H}_9\text{O}_2$; 1,3-dihydroxybenzene)
VAN	Vanillic acid ($\text{C}_8\text{H}_{10}\text{O}_4$; 1-carboxy 3-methoxy 4-hydroxy benzene)
C6-SYR	Syringic acid ($\text{C}_6\text{H}_{13}\text{O}_5$; 1-carboxy 3,5-dimethoxy 4-hydroxy benzene)
DBA	3,5-dimethoxy benzoic acid ($\text{C}_6\text{H}_6\text{O}$)
SR-RO	Suwannee River Reverse Osmosis isolate
CR	Nanofiltration isolate from the Central Arizona Project

W-NF

C6: Represents benzene rings

Table 7.2- Halogen reaction with alum coagulated CRW water.

Alum Dose ppm	Bromine Addition			Chlorine Addition		
	Br ₂ Consumed (μM)	CHBr ₃ Produced (μM)	CHBr ₃ / Br ₂ Consumed (μM/μM)	Cl ₂ Consumed (μM)	CHCl ₃ Produced (μM)	CHCl ₃ / Cl ₂ Consumed (μM/μM)
25	41	0.565	0.0139	39	0.217	0.00559
50	34	0.393	0.0115	--	--	--
100	28	0.261	0.0094	35	0.0617	0.00175
150	24	0.240	0.0101	35	0.0601	0.00171
200	19	0.203	0.0105	32	0.0469	0.00148
250	19	0.205	0.0106	--	--	--

Table 7.3- Pseudo zero-order and pseudo first order rate constants of bromine reaction with NOM (initial Br₂ (aq)= 2 μM, pH 5, and temperature 24 °C).

NOM source/treatment	Pseudo zero-order (Δ halogen 15 seconds in μMs ⁻¹)			Pseudo first-order
	DOC concentration 20μM,	50μM,	100 μM, 150μM	Average (s ⁻¹)
SR-RO	0.047, ----	0.091,	0.136,	1.85×10^{-3}
Pre-ozonated	0.037,	0.068,	0.105,	1.26×10^{-3}
SR-RO	0.117			
CRW-NF	0.023, 0.077	0.040,	0.060,	7.71×10^{-4}
Pre-ozonated	0.020,	0.029,	0.036,	5.61×10^{-4}
CRW-NF	0.047			

Table 7.4- Pseudo zero-order and pseudo first order rate constants of chlorine reaction with NOM (initial Cl_2 (aq)= 2 μM , pH 5, and temperature 24 °C).

NOM source/treatment	Pseudo zero-order (Δ halogen 15 seconds in μMs^{-1})			Pseudo first-order
	DOC concentration 20 μM , 50 μM , 100 μM ,	150 μM	Average (s^{-1})	
SR-RO	1.33×10 ⁻³ , 5.00×10 ⁻³	1.90×10 ⁻³ , 3.40×10 ⁻³ ,	4.30×10 ⁻⁵	
Pre-ozonated	7.67×10 ⁻⁴ ,	1.33×10 ⁻³ , 2.50×10 ⁻³ ,	2.89×10 ⁻⁵	
SR-RO	3.83×10 ⁻³			
CRW-NF	6.67×10 ⁻⁴ , 3.87×10 ⁻³	1.17×10 ⁻³ , 1.93×10 ⁻³ ,	2.54×10 ⁻⁵	
Pre-ozonated	5.00×10 ⁻⁴ ,	9.00×10 ⁻⁴ , 1.23×10 ⁻³ ,	1.66×10 ⁻⁵	
CRW-NF	1.67×10 ⁻³			

Table-7.5- Rate constants of HOBr and HOCl (pH 5).

NOM source/treatment	$K_{\text{HOBr}} (\text{M}^{-1}\text{s}^{-1})$		$K_{\text{HOCl}} (\text{M}^{-1}\text{s}^{-1})$	
	10 °C	24 °C	10 °C	24 °C

CRW-NF isolate	27	31	1.6	1.7
Pre-ozonated CRW-NF isolate	---	15	---	0.70
SR-RO isolate	120	130	4.3	4.86
Pre-ozonated SR-RO isolate	---	76	---	2.27

Table 7.6- SUVA for untreated or treated (e.g., pre-ozonation, bromination, or chlorination) CRW-NF and SR-RO isolates.

NOM Source/ treatment	SUVA ₂₅₄ (m ⁻¹ [mg/L] ⁻¹)
CRW-NF	1.3
CRW-NF with pre-ozonation	0.8
SR-RO	4.2
SR-RO with pre-ozonation	2.4
SR-RO with HOBr addition	3.9
SR-RO with HOCl addition	2.2

Table 7.7- Percentage area beneath ranges of ¹³C-NMR wavelengths for untreated CRW-NF and untreated, chlorinated, and brominated SR-RO isolates.

NOM Source/ treatment	¹³ C-NMR chemical shift range (%)						
	0-62 ppm	62-90 ppm	90-110 ppm	110-140 ppm	140-160 ppm	160-190 ppm	190-230 ppm
	Aliphatic	Aliphatic	Anomeric	Aromatic	Aromatic/p henolic	Carboxylic	ketone
CRW-NF	55	13	1.7	6.9	2.5	20.3	1.4
SRRO	32	19	9.3	14	6.9	16	3.9
SRRO+ HOCl	37	28	7.8	7.6	3.7	18	0
SRRO+ HOBr	33	21	9.5	13	6.0	15	2.6

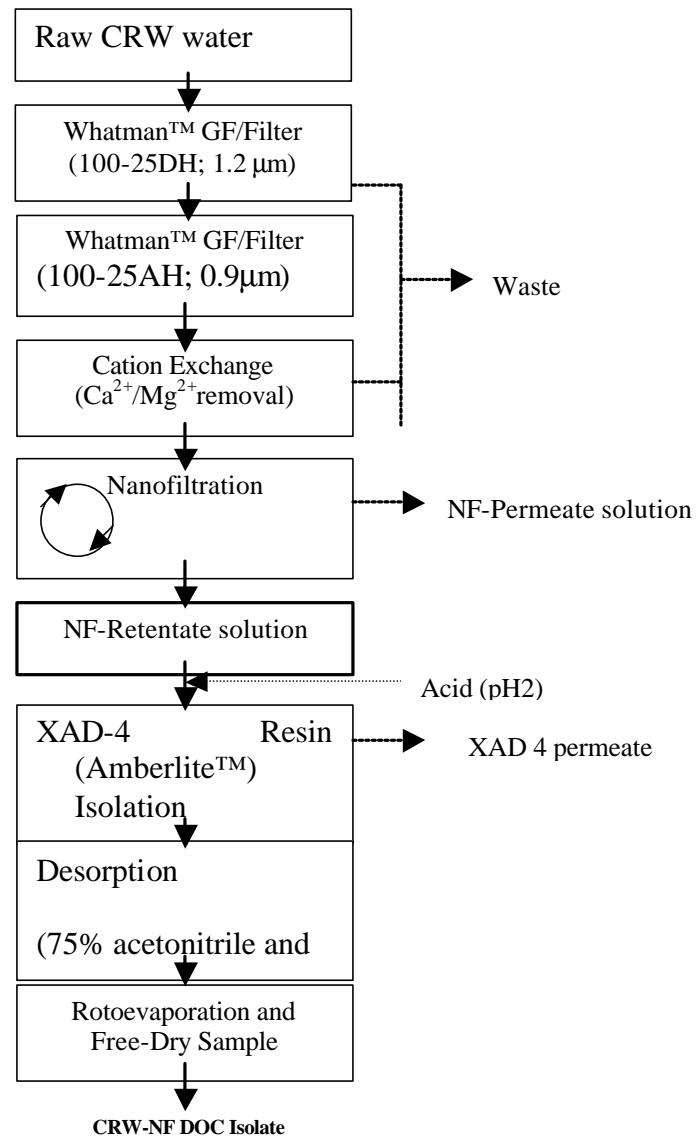


Figure 7.1 - Schematic of raw CRW water nanofiltration and XAD 4 isolation system.

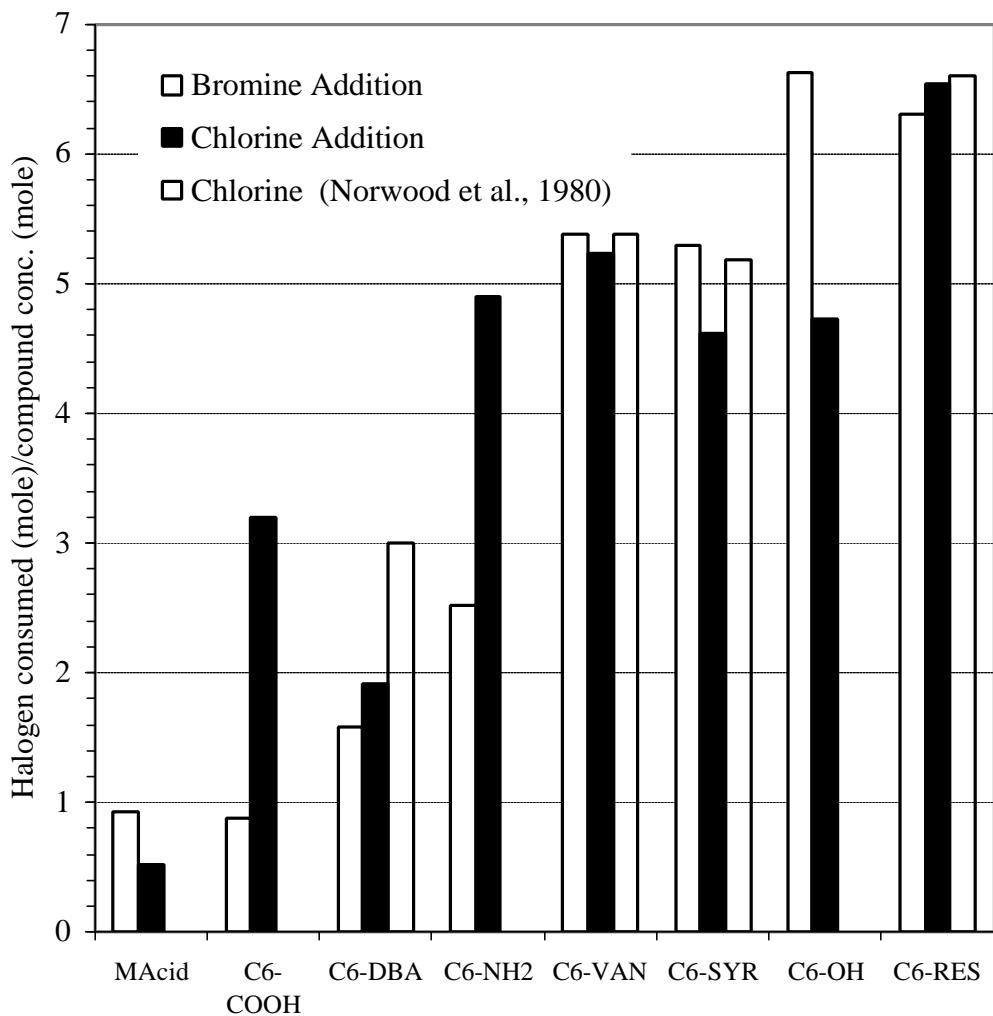


Figure 7.2 - Bromine or chlorine consumption with reaction model organic compounds.

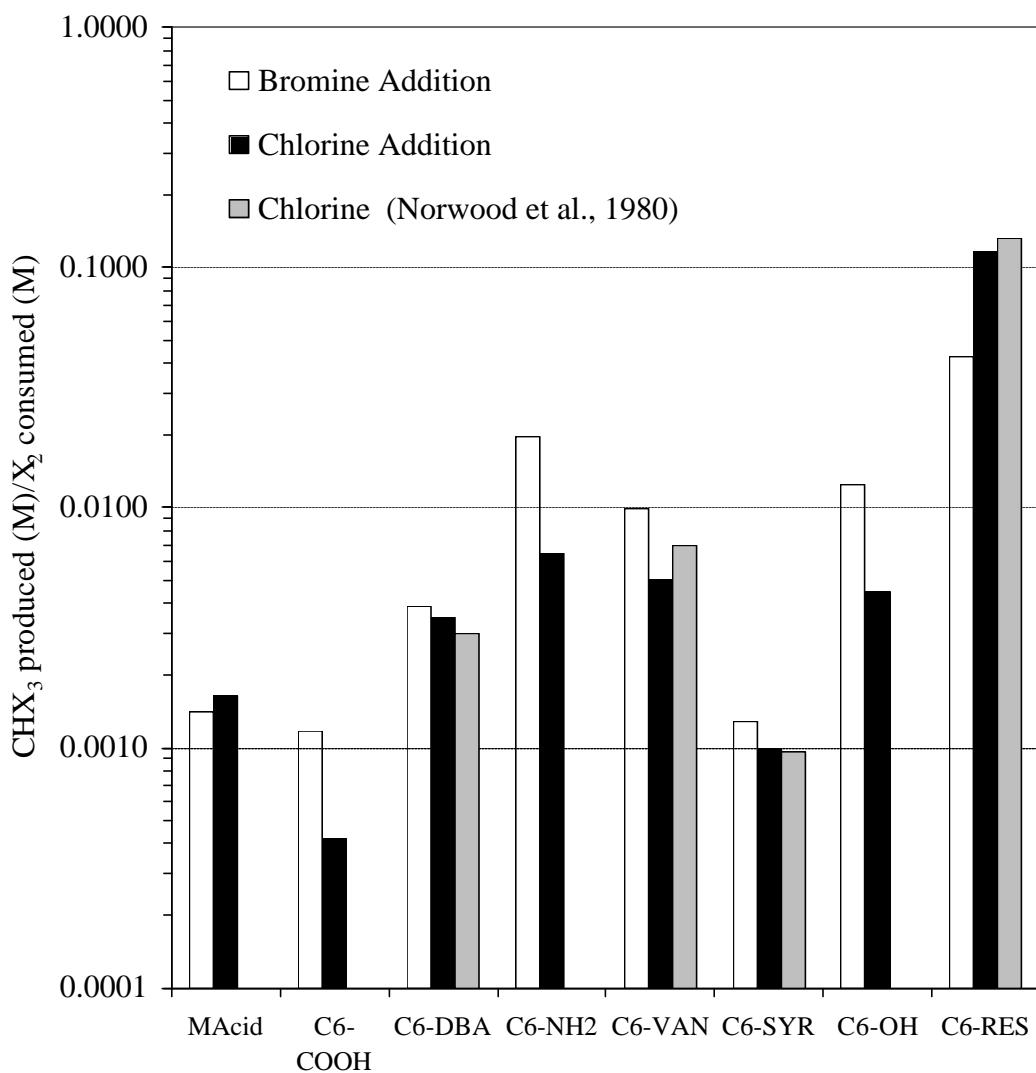


Figure 7.3- Haloform formation for model organic compounds reaction with bromine or chlorine.

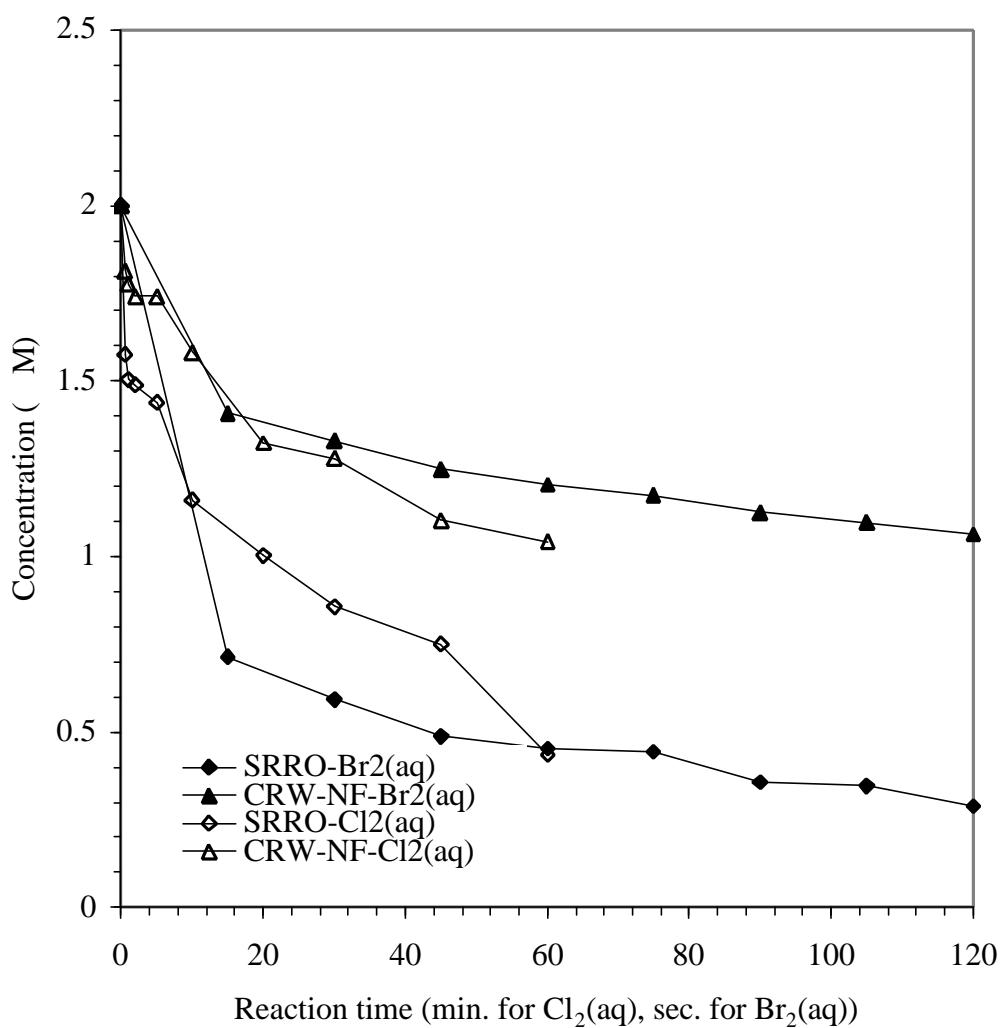


Figure 7.4- Kinetic reaction of aqueous bromine and chlorine with SRRO isolate and CRW-NF (conditions: initial $[Br_2(aq)] = [Cl_2(aq)] = 2\mu M$; pH=5; $[DOC] = 50 \mu M$ as C).

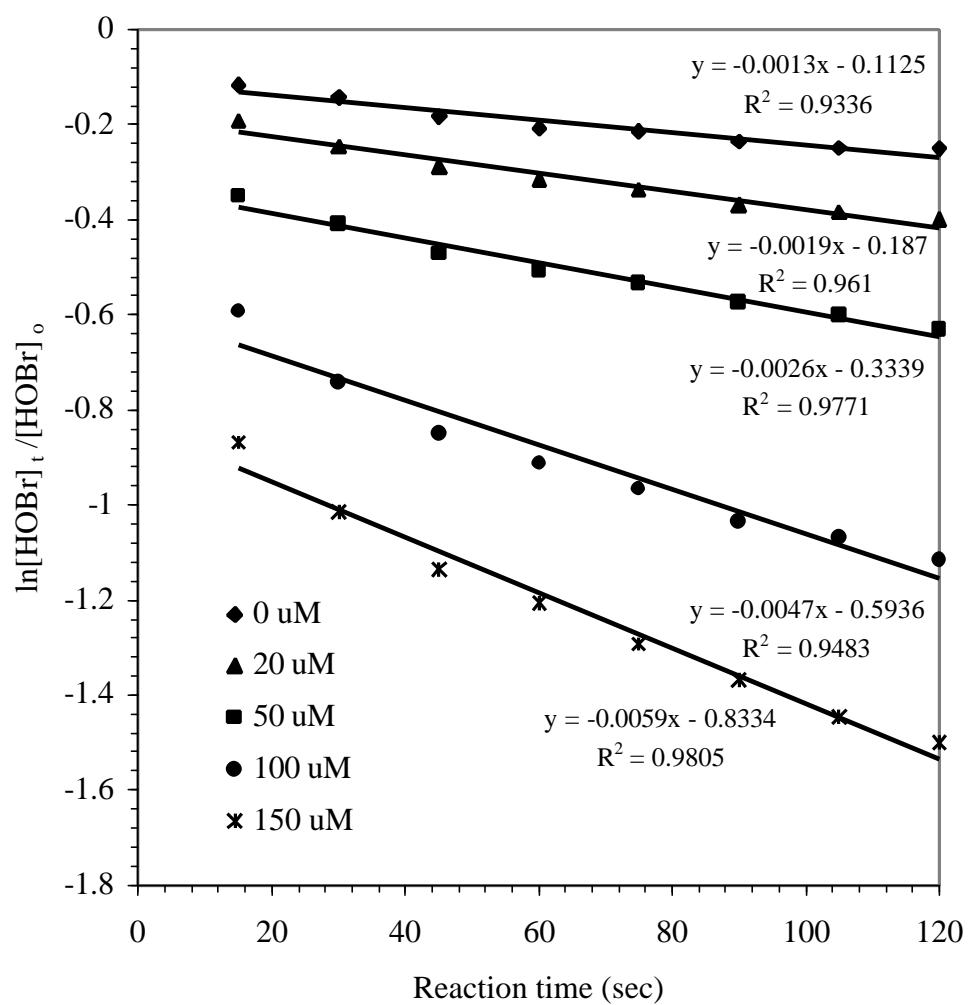


Figure 7.5- First-order rate constants (k') of bromine reaction with NOM
(conditions: pH 5; temperature: 24°C; DOC: CRW-NF isolate).

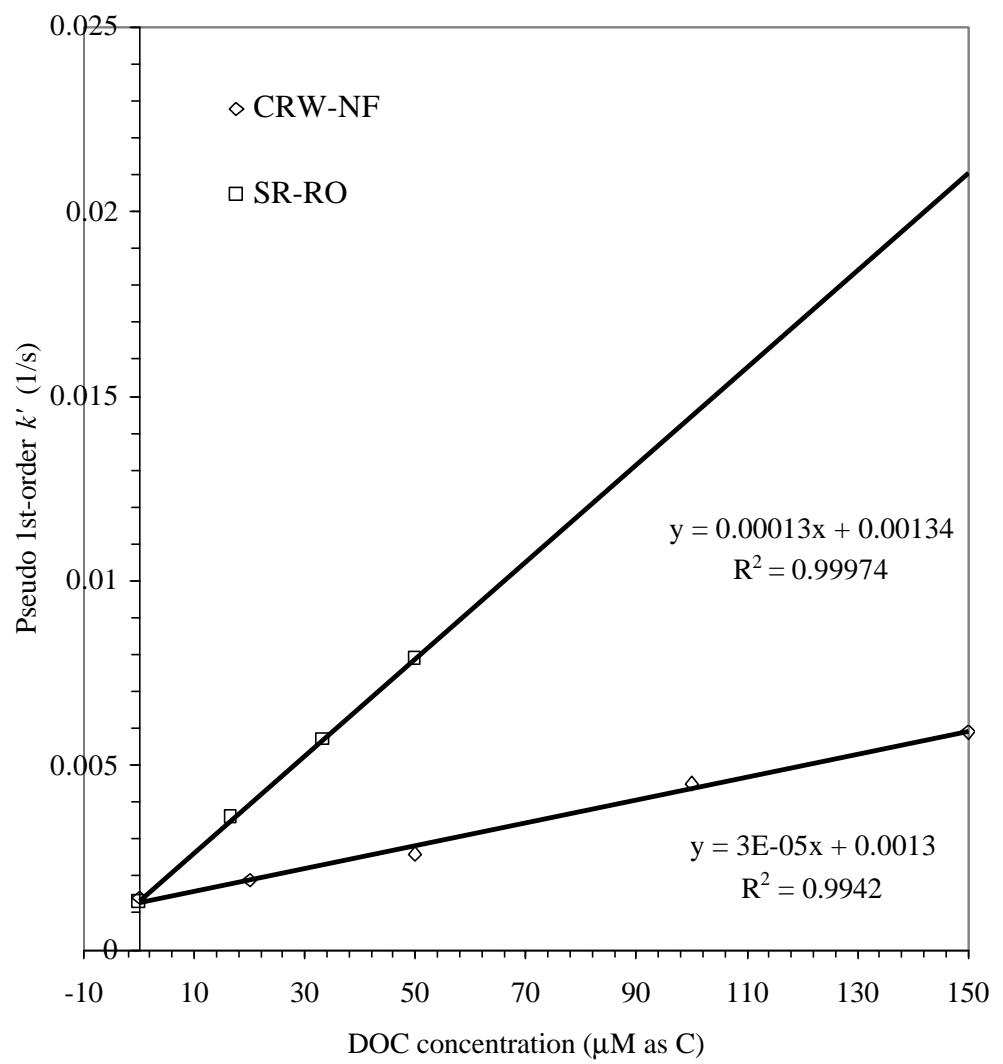


Figure 7.6- Pseudo first-order rate determination for CRW-NF or SR-RO isolate reaction
with bromine (slop represents 2nd order rate constant in $\mu\text{M}^{-1}\text{s}^{-1}$; conditions:
pH 5, temperature: 24°C)

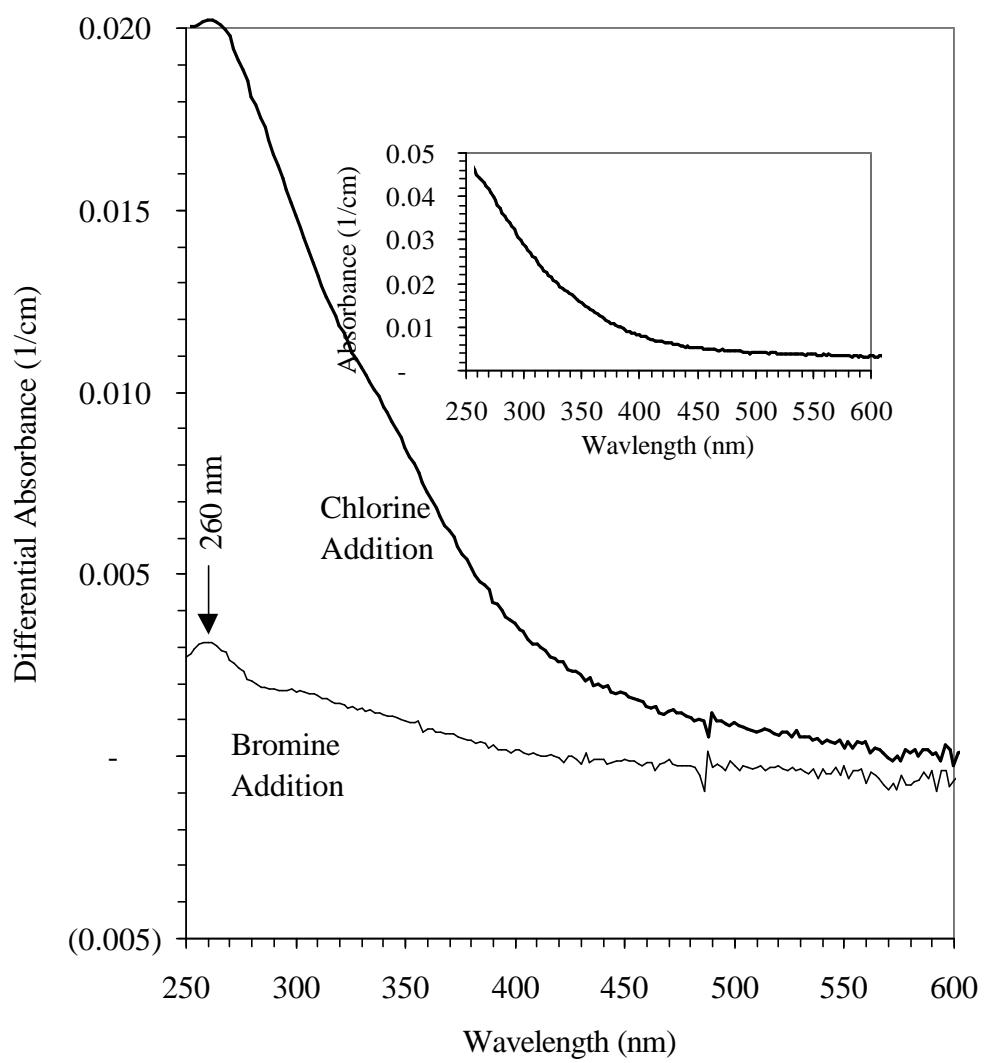


Figure 7.7- Differential UV/VIS spectra for SR-RO reaction with bromine or chlorine
(inset: UV/VIS spectra for SR-RO at DOC: 1 mg/L).

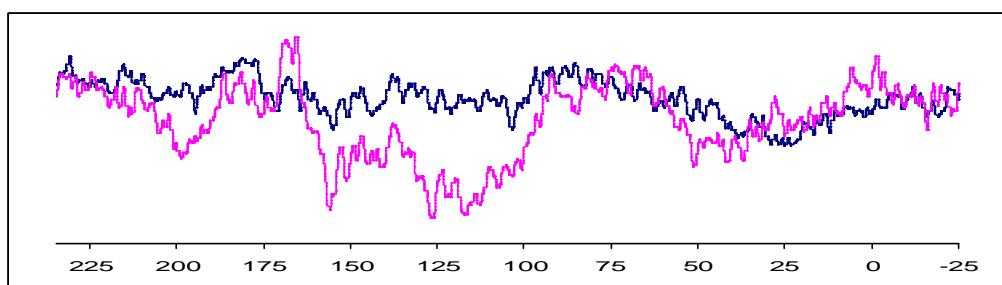
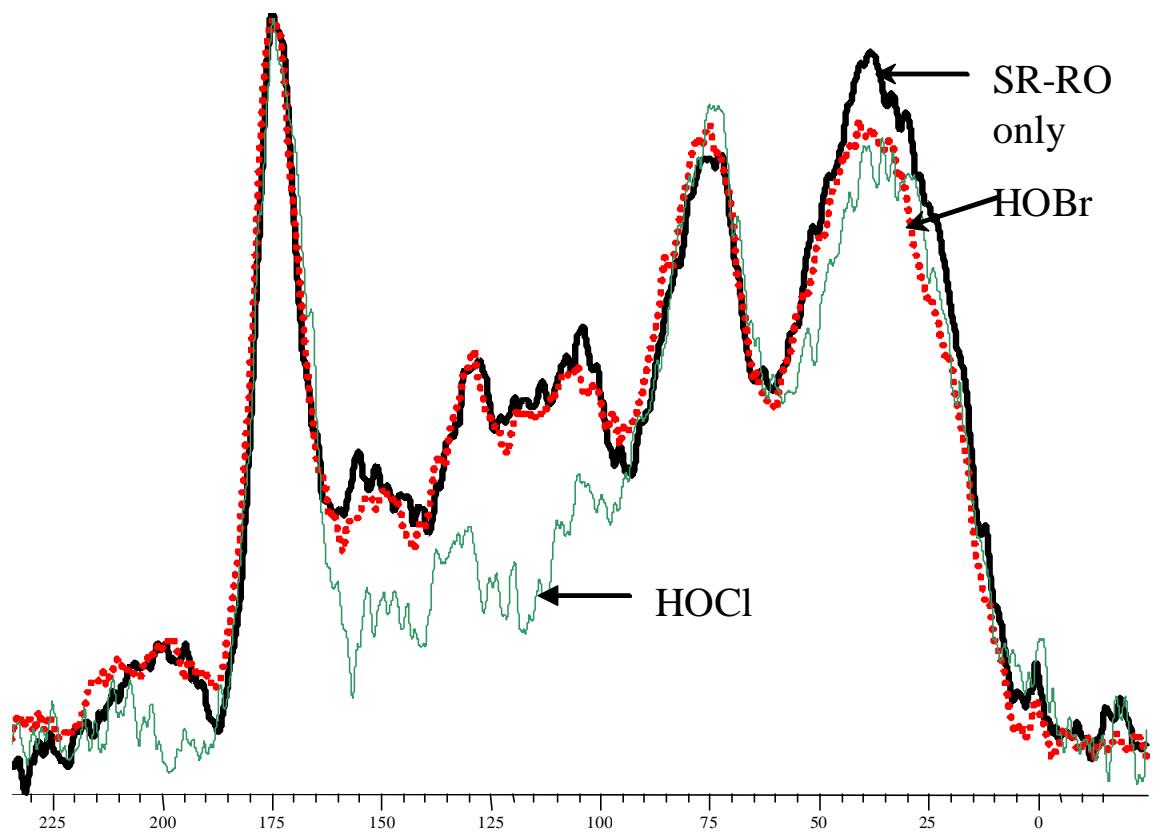


Figure 7.8- ^{13}C -NMR (upper) and differential spectra (lower) spectra of SR-RO NOM isolate.

19. CHAPTER 8

20. SUMMARY AND CONCLUSIONS

This chapter consists of three sections, including 1) synthesis of this study, 2) conclusions, and 3) recommendations. Section 8.1 describes the motivation for the aspects of this study and addresses the four hypotheses based upon the ozonation and halogenation experimental results. Section 8.2 summarizes the conclusions and findings from the four major tasks, including:

- 1) Task 1: Develop a comprehensive kinetic database of molecular ozone exposures and HO[•] concentrations during ozonation of natural waters (Chapter 4);
- 2) Task 2: Quantify effects of water quality and treatment variables on bromate formation (Chapter 5);
- 3) Task 3: Evaluate ammonia addition for bromate control (Chapter 6);
- 4) Task 4: Determine reaction rates and DBP formation between aqueous bromine or aqueous chlorine reaction with NOM (Chapter 7).

In addition, a short recommendation in Section 8.3 is incorporated to suggest the use of ozonation and bromate formation control strategies.

20.1. 8.1 SYNTHESIS OF THIS STUDY

After research in the early 1990's, a consensus exists for the formation mechanisms that bromate formation depends upon oxidation reactions involving both O₃ and HO radicals. The purposes of this research were to provide a through investigation of effects of natural water constituents and water treatment variables on ozone decomposition, HO[•] production and bromate formation. Three key issues, which are lacking from previous studies, were especially focusing on as follows:

- Effects of HO[•] concentrations and ratio of oxidant pathways (O₃/HO[•]) on bromate formation in natural waters.
- Effects of aqueous bromine scavenging by ammonia on bromate formation.
- Effects of aqueous bromine scavenging by NOM on bromate formation.

In addition to ozonation study, since aqueous bromine is also an important intermediate affecting THM and HAA formation during chlorination of bromide-containing waters, investigation of reactivity between halogen (e.g., chlorine and bromine) and NOM was included in this study.

20.1.1. 8.1.1 Ozonation of Colorado River Water

During ozonation process of waters containing bromide, ozone decomposition, HO[•] production and bromate formation were affected by some water quality parameters and treatment variables. The CRW water was selected as a representative of natural waters since it is a major water supply for the six southwestern states, and many water treatment plants using CRW are, or will be, practicing ozonation. Based upon the baseline water quality of CRW water, each of the selected parameters was adjusted to different levels to simulate its change of concentration while maintaining other parameters constant. It was observed that the R_{CT}, expressed as ratio of HO[•] concentration (or exposure) versus ozone concentration (or exposure) remained unchanged during the entire ozonation process and thereby ozone concentrations and HO[•] concentrations can be quantified throughout the overall process.

In general, effects of individual water quality parameter on ozone exposure, R_{CT} and HO[•] exposure showed trends that most water quality parameters had negative impact on ozone exposure except (bi)carbonate alkalinity (Table 8.1). Water quality parameters such as pH, temperature, and DOC had positive influence on R_{CT}, but showed negative impact for bromide and (bi)carbonate alkalinity. The HO[•] concentrations (or exposures) increased with increasing water pH, temperature and DOC, but decreased with lower bromide and (bi)carbonate alkalinity.

The Hypothesis II states that HO[•] concentrations decrease proportionally with increasing DOC and (bi)carbonate alkalinity and decreasing pH in natural waters. The followings list the supporting and rejecting evidences:

- Figure 8.2 shows that HO[•] exposures decrease proportionally with increasing (bi)carbonate alkalinity, but increase with increasing pH and DOC in natural waters. Similar trends for HO[•]

concentrations that perform proportionally with water pH, (bi)carbonate alkalinity and DOC levels at the same ozone residuals .

- Since inorganic carbon species are active to HO[•] but inert to molecular ozone, increasing water (bi)carbonate alkalinity results in increasing capability of scavenging HO[•], and thus decreases in HO[•] concentration. On the other hand, HO[•], formed via the reactions of ozone and hydroxide ions, decreases with decreasing water pH due to the decrease of hydroxide ions concentration at lower pH.
- The results show that, in contrast to the Hypothesis II, HO[•] concentrations slightly increase by approximately 25% as increasing DOC concentrations from 3 mg/L to 4.5 mg/L (Figure 5.13). R_{CT} increased at higher initial DOC concentrations, but ozone exposure decreased. Therefore, overall higher HO[•] concentrations occurred with increasing DOC due to initiation of ozone decomposition by NOM.

The HO[•] concentrations and R_{CT} affect bromate formation. Responses in the extent of bromate formation for variable water quality and treatment conditions from the literature include the followings:

- Initial bromide level, pH, temperature, and (bi)carbonate alkalinity increased effects on bromate formation;
- DOC and ammonia decreased bromate formation.
- Treatment variables such as ozone dose (expressed as C), contact time (expressed as T), and exposure of C×T perform positive effects on bromate formation.

The Hypotheses I expresses that bromate formation increases proportionally to the ratio of [HO[•]]/[O₃] during ozonation and is affected by different water qualities and water treatment conditions. Based upon this study, evidences of supporting the hypothesis are listed below:

- By plotting linear regressions of R_{CT} against rates of bromate formation as functions of water quality parameters and treatment variables, R_{CT} showed linear relationships with rates of bromate formation. Table 8.2 summaries the degrees of correlations between R_{CT} and rates bromate formation. Whereas R_{CT} expresses the molar ratio of oxidants (HO[•]/O₃) for bromide oxidation to bromate, the specific ozone and HO[•] concentrations define the amount of oxidant present in ozonated waters.

- Although linear relationships were observed between R_{CT} and rates of bromate formation, positive relationships between R_{CT} and bromate formation rates occurred on varying water pH and temperature, whereas, on the other hand, negative relations were found for bromide, (bi)carbonate alkalinity, DOC and ozone dose. In addition, R_{CT} was not affected by ammonia while decreasing rates of bromate formation. These can be concluded, in general, that different water quality constituents and treatment conditions play different roles on affecting ozone decomposition, HO^\bullet production as well as chemistry of bromate formation. Therefore, utilities concerned both bromate formation and oxidation/disinfection performance need gain knowledge of R_{CT} in their ozonation systems to better address ozone application strategies.

Among bromate formation chemistry during ozonation processes, HOBr/OBr^- is the critical reaction intermediate from where several reaction pathways are possibly occur:

- To reaction with NOM and form brominated organic compounds,
- To further oxidize to form bromate, and
- To react with ammonia to form bromamines.

Formation of bromate can be reduced if the intermediate species are being controlled. Both ammonia and NOM can react with aqueous bromine that once formed from bromide oxidation during ozonation and thus inhibit to further oxidation to bromate (Figure 8.1). While NOM can also react with ozone and HO^\bullet , ammonia only performs negligible interaction with ozone and HO^\bullet . Ammonia can block bromate formation by scavenging OBr^- , thus impede OBr^- from further oxidation to form bromate via intermediate BrO_2^- or BrO^\bullet species by direct molecular ozone and indirect HO^\bullet . However, bromate formation via indirect HO^\bullet pathways cannot be interfered by ammonia. Ammonia addition diminishes bromate formation via direct and direct/indirect pathways, and resulted in major bromate formation by indirect HO^\bullet pathways. On (bench- and pilot scale) continuous flow ozonation for R_{CT} , water quality variables and ammonia addition tests validated batch experimental work to support the hypothesis III that “ammonia addition for controlling bromate formation does not alter the $[\text{HO}^\bullet]/[\text{O}_3]$ ratio, but shifts bromate formation towards the HO^\bullet oxidation pathway by scavenging HOBr/OBr^- .”

20.1.2. 8.1.2 Halogenation (Bromine or Chlorine Reactions with NOM)

Reactivity of aqueous bromine or chlorine reactions with NOM is dependent upon characteristics of NOM (e.g., aromatic content and functional groups). Kinetic reactions of halogen with NOM showed that NOM performed a two-stage of reaction sites: a fast stage reaction site then followed by a slow stage reaction site. Rate constants for the slower stage of bromine with NOM and chlorine with NOM were 30 to 130 M¹s⁻¹ and 1 to 5 M¹s⁻¹, respectively depending upon characteristics of NOM (22 °C). Aqueous bromine reactions with NOM appear to be much faster than does chlorine by approximately one order of magnitude and, therefore, supported the Hypothesis IV that “aqueous bromine reacts faster with NOM than aqueous chlorine and the rate of reaction between bromine and chlorine with NOM is affected by the characteristic of NOM. However, reactions of bromine or chlorine with slower reaction sites appear to similar order of magnitude between pH 5 through 11. This implies that both protonated and deprotonated NOM participate in reactions with HOBr and OBr⁻ (HOCl and OCl⁻).

20.2. 8.2 CONCLUSIONS

This study has determined effects of a wide range of water quality variables and treatment conditions on ozone decomposition, HO[•] concentrations as well as bromate formation. In addition, a study of the reactivity and DBP formation between the reactions of bromine or chlorine with NOM was also conducted. The followings summarize the results from this study:

- 1) Batch ozonation experiments showed a three-stage of ozone consumption, defined as instantaneous stage, fast stage, and slow stage, whereas only a slow stage ozonation was observed at bench- and pilot-scale continuous flow ozonation.
- 2) During ozonation of water with a set of water quality and treatment conditions, a two-stage R_{CT}, expressed as a fast stage then followed by a slow stage, was defined. The values of R_{CT} were

affected by water quality parameters and treatment variables. In general, R_{CT} values at the fast stage were higher than at the slow stage by a factor of 2 to 3. R_{CT} increased with increasing water pH, temperature, and concentration of DOC. R_{CT} decreased with decreasing bromide and (bi)carbonate alkalinity levels. Decreasing initial ozone dose resulted in increase of the R_{CT} . Depression of water pH decreased the R_{CT} values. Ammonia addition to control bromate, however, did not alter the R_{CT} , up to the concentration of 0.5 mg-N/L.

- 3) The values of R_{CT} for ozonation of CRW water were within the range between 10^{-7} to 10^{-9} (M/M or M-min/M-min), resulting in the HO^{\bullet} concentrations on the order of 10^{-12} to 10^{-14} moles per liter (M) during most ozonation conditions (3-5 mg- O_3 /L).
- 4) Ozone dose, initial bromide concentration, pH, temperature, and (bi)carbonate alkalinity act positive effects on bromate formation, while the presence of natural organic matter (NOM) and ammonia lower the amount of bromate formed. Values of R_{CT} show a linear relationship with bromate formation. Table 8.1 summarizes general impacts on ozone exposure, HO exposure, R_{CT} values and bromate formation by the above parameters.
- 5) Ammonia can effectively reduce bromate formation; however, the efficiency is lessened with lowering water pH. Stoichiometricly, when the molar ratio of $\text{NH}_4^+/\text{Br}^-$ is greater than 15, up to 60% and 85% of bromate reduction can be achieved at pH 7.5 and 8.5, respectively, whereas no observed bromate reduction at pH lower than 6.5.
- 6) Based upon bromate formation pathways (e.g., direct Q_1 versus indirect HO^{\bullet}), intermediate aqueous bromine can be inhibited by reacting with ammonia to prevent further oxidation via both direct/indirect and direct oxidation pathways. Ammonia, however, cannot totally inhibit bromate formation even applying an excess stoichiometric ammonia dose unless indirect HO^{\bullet} radicals bromate formation pathways can be controlled.
- 7) Reactivity of NOM with chlorine or bromine study shows that an indirect UV Absorbance method using ABTS as an indicator can provide a useful tool in determining rapid kinetic reactions of chlorination and bromination.
- 8) Kinetically, bromine reaction with NOM is nearly one order of magnitude faster than similar chlorine reactions. Both HOBr and OBr^- (or HOCl and OCl^-) appear to participate in reacting with

- NOM; however, HOCl acts as a stronger oxidizing agent with NOM than does HOBr, which is substituting agent. In addition, halogen consumption and haloform formation is dependent on the characteristics of the NOM (e.g., aromatic content and functional groups).
- 9) Bromine reaction rate constants for non-ozoneated NOM were 30 to 130 M⁻¹s⁻¹, and 15 to 75 M⁻¹s⁻¹ for pre-ozoneated NOM, whereas chlorine reaction rate constants for non-ozoneated NOM were 1 to 5 M⁻¹s⁻¹, and 1 to 2 M⁻¹s⁻¹ for pre-ozoneated NOM.
 - 10) Kinetically, the impact of bromate reduction by the reaction of intermediate HOBr and NOM is only important during the fast ozonation stage ($t < 2$ minutes). A negligible impact on bromate reduction by HOBr and NOM reactions at slow ozonation stage ($t > 2$ minutes) can be implied based upon the rate constants and reactivity of NOM.

20.3. 8.3 RECOMMENDATIONS

As drinking water quality gradually becoming more stringent to minimize the risk of the public health, advanced treatment technologies such as ozone and membranes have become more feasible to lower the MCLs of toxic constituents. On the other hand, even though the treated waters meet the drinking water standards, consumers are usually more concerned on their waters' aesthetics and judge the water quality based on its flavor, odor or color.

The use of ozone as one of the treatment processes can provide a number of benefits in terms of drinking water treatment (Table 8.2). Therefore, it can be considered an alternative treatment technology to meet the future regulation. Ozone does not only perform as a powerful disinfectant that can easily inactivate viruses, bacteria and even chlorine-resistant *Cryptosporidium* pathogens, but also can provide a series of water treatment benefits such as oxidation of problematic metals, removal of organic DBP precursors and taste and odor compounds, increasing biodegradability of organics before GAC filtration. Recent concerned endocrine disruptors and pharmaceutical compounds, pesticides and herbicides, or even organic petroleum additives and industrial solvents can be removed by ozonation. However, ozone application has its disadvantages compared to other disinfectants/oxidants (Table 8.2). High operation and maintenance costs and bromate formation are probably the keys that determine the application and these factors are strongly dependent upon the source water quality.

Since both ozone and HO[•] perform the treatment benefits, knowing the rate of ozone decay and HO[•] concentrations are crucial before predictions of the efficiency of removing selected constituents, bromate formation, health effects, and cost of regulatory compliance. While ozone residuals can be readily measured, addition of PCBA into water prior to ozonation reactor might not practical in full-scale water treatment plant to determine HO[•] concentrations. A surrogate HO[•] probe such as MIB, geosmin, or atrazine that already exists in waters can be a candidate to measure HO[•] concentrations after calibration with the reaction with ozone. Once the R_{CT} databases have been developed for any particular source water, the concentrations of O₃ and HO[•] can be determined, and therefore, the ability of disinfection/oxidation as well as formation of DBPs could be predicted.

While the benefits of ozonation are numerous, the production of DBPs must also be considered. Although a number of non-halogenated DBPs have been found after ozonation of waters that contain bromide (Richardson et al., 1999), bromate is the major concerned DBP since it has been shown as a likely human carcinogen. Based on its status, bromate has been regulated in the United States by the Stage I Disinfectants/Disinfection By-Products Rule at 10 µg/L (EPA, 1998). Under the typical risk-assessment conditions (A 70-kg adult consuming 2 L of water per day for 70 years), the EPA calculated that a 10 µg/L bromate concentration results in a lifetime cancer risk of greater than 10⁻⁵. Therefore, as gradual improvement of analytical technology, future regulation of bromate could be lower.

However, balancing between ozone provided benefits and DBP formation could be very challenging. While attempting to strengthen the ozone performance of removing toxic constituents, bromate formation can easily exceed the MCL even if waters only contain trace bromide. For those source waters that have historical high bromide levels, the application of ozone might not be practical if the high bromate formation cannot be addressed. In general, bromate formation can be effectively controlled by addition of acid. For waters that have high pH but low (bi)carbonate alkalinity, pH depression prior to ozonation can be economically feasible to control bromate below the MCL. On the other hand, ammonia

has been shown to effectively reduce formation of bromate during ozonation processes. In general, adding less than 0.5 mg-N/L of ammonia can perform maximum efficiency on bromate reduction without altering ozone's disinfection/oxidation capability and forming observable amount of nitrate. For waters that already contain ammonia, bromate formation can be probably controlled without adding additional ammonia. Furthermore, addition of ammonia in pre-ozonated waters might be beneficial to reduce formation of some chlorinated carcinogenic DBPs (e.g., trihalomethanes and haloacetic acids) when chlorine is applied for microorganisms control in the distribution systems.

Table 8.1- Trends of ozone exposure, HO[•], the R_{CT} and bromate formation on water quality parameters and treatment variables during ozonation.

Parameter	Values	O ₃ -CT	HO [•] -CT	R _{CT}	Rate of bromate formation
Bromide		↓	↓↓	↓	-
pH		↓	↑↑	↑	↑
Temperature		↓	↑	↑	↑
Alkalinity	-	↑	↓↓	↓	↑
DOC		↓	↑	↑	↓
Ammonia	unchanged		unchanged	unchanged	↓
Ozone dose		↑	↑	↓	↑

Table 8.2- Correlations between R_{CT} and bromate formation rate as functions of water quality parameters and treatment variables during ozonation.

Parameter	Values	R ² of R _{CT} versus rate of BrO ₃ ⁻ formation (Fast stage/Slow stage)
Bromide		0.91/0.75
pH		0.90/0.99
Temperature		0.99/0.92
Alkalinity	-	0.80/0.88
DOC		0.99/0.99
Ammonia		---
Ozone dose		0.93/0.96

Table 8.3- Advantages and disadvantages of using ozone for drinking water treatment.

Advantages	Disadvantages
<ul style="list-style-type: none"> • Effective inactivation of bacteria, viruses, Giardia, and Cryptosporidium • Oxidation of iron, manganese, and sulfides • Effective control of taste, odors and color • Enhancement of clarification process and turbidity removal • Short contact time • Not causing chlorinated DBPs problems 	<ul style="list-style-type: none"> • Forming brominated DBPs (e.g., bromate and bromine-substituted DBPs) in the presence of bromide • High operation cost and should be generated on-site • Ozone is highly corrosive and toxic • No residual provided

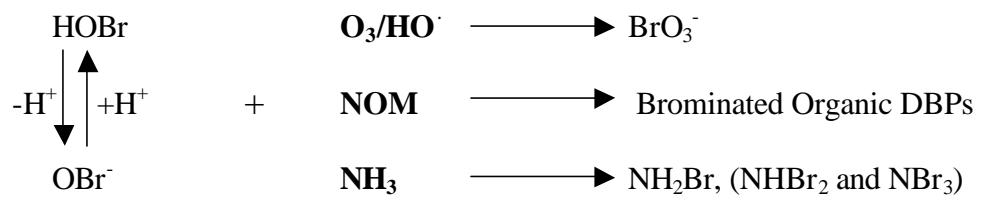
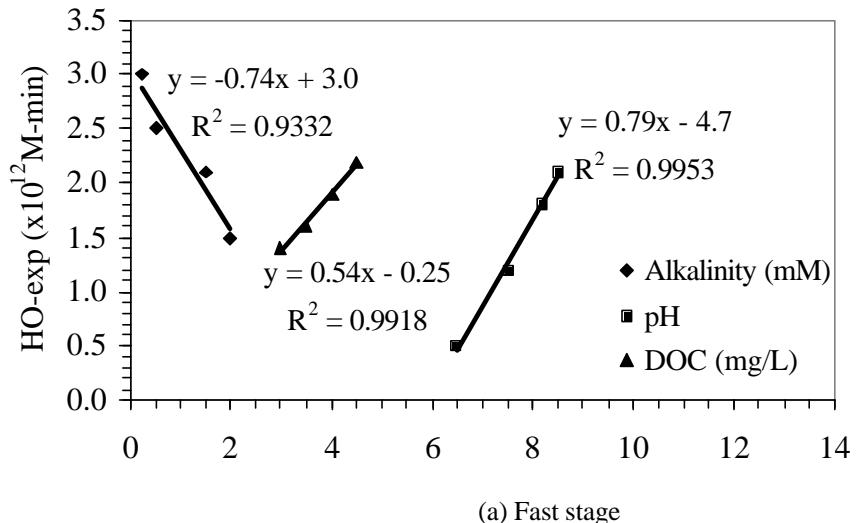
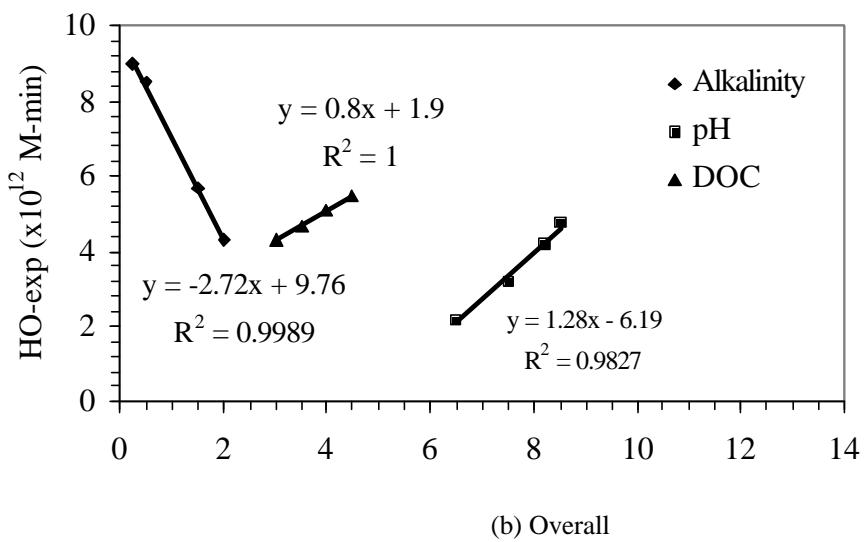


Figure 8.1 - Reactions pathways of aqueous bromine with ozone, HO^\bullet , NOM and ammonia.



(a) Fast stage



(b) Overall

Figure 8.2- Correlations of HO[•] exposures (or concentrations) with alkalinity, pH and DOC: (a) fast stage (< 2 minutes); (b) overall of ozonation (20 minutes).

21. APPENDIX A

22. CRW DISSOLVED ORGANIC CARBON ISOLATION PROCESSES

Water Sample Preparation CAP water will be the single water source used for all ozonation experiments. The raw water will be collected from CAP canal in Scottsdale Water Campus and then filtered with 0.7- μm pore diameter filter papers (GF/F, Whatman™) then stored at 4 °C when not in use to minimize water quality changes. All reagents are analytical grade and the chemical solutions will be prepared periodically to maintain freshness and minimize decay.

Procedure for NOM Isolation

The purpose of this CAP raw water DOC extraction work was to obtain CAP DOC isolate for adjusting DOC concentrations for some of the ozonation kinetics experiments and for use as one of the two NOM sources for the chlorine/bromine reaction with NOM kinetic experiments. The other DOC source was a Suwannee River raw water DOC isolated by reverse osmosis technique obtained from International Humic Substance Society (IHSS).

There are six processes required for extracting approximately 2 grams of DOC isolate out of 800 liters. The schematic procedure of CAP raw water DOC isolation is shown in Figure 5.1. The sample water was first filtered through Balston Whatman Glass Fiber filters DH (2.5 μm pore size) and AH (0.9 μm pore size) in series to remove particulate matter. Before water went through the Nano-filtration system, hardness removal (Ca^{2+} and Mg^{2+}) was performed by ion exchange using Na^+ -saturated resins (Barnstead-Thermoclyne D8904). Flow rates for both processes were controlled at $2 \pm 0.2 \text{ L/min}$. DOC concentrate by Nano-filtration was conducted by NF-70 membrane with molecular weight cutoff of 500-dalton. The concentrate at the influent and permeate at the effluent were collected to determine DOC concentration and UV Absorbance. The concentrate (20L) was collected for further isolation by an Amberlite™ XAD-4 resin column. Mass balance analyses show approximately 90% of sample was recovered. After the XAD-4 isolation process, the acetonitrile and residual formate in concentrate were removed by rotoevaporation and the volume of the concentrate was reduced down to 2-4 liters. The final DOC isolate was obtained after freeze-drying for removing residual solvents. The DOC isolates were characterized by $^{13}\text{C-NMR}$ spectroscopy. The overall isolation processes were completed in August 1999 and the isolates were stored in a dessicator.

23. APPENDIX B

24. TRACE TESTS OF CONTINUOUS FLOW OZONAITON

Trace tests of bench-scale continuous flow ozonation were conducted to determine the hydraulic flow conditions. A blue-dye solution was added at the influent port prior to ozone reactors. Residence time distribution analysis was carried out by monitoring the UV absorption at wavelength of 600 nm of the solution collected at sampling Port 1 and 2. Table B1 shows a summary of flow conditions.

Table B1 - Summary of trace tests for bench-scale continuous flow ozonation reactors

Conditions	Port 1	Port 2
Hydraulic retention time (min)	4.6	9.4
Mean residence time	5.5	11
Number of CSTRs calculated	5	8