

**KINETIC-BASED MODELS FOR BROMATE FORMATION  
IN NATURAL WATERS**

**USEPA GRANT # R 826835-01-0**

**FINAL REPORT – EXECUTIVE SUMMARY**

Investigator:

Paul Westerhoff, Ph.D., PE  
Associate Professor  
Department of Civil and Environmental Engineering  
Arizona State University  
Tempe, AZ 85287

July 2002

**EPA STAR Agreement Number:** R 826835-01-0  
**Project Period:** December 15, 1998 – December 14, 2001  
**Research Category:** Drinking Water: Disinfection By-Products (DBP Modeling)

## EXECUTIVE SUMMARY

Ozonation is currently considered one of the most effective microbial disinfection technologies (Finch et al., 1994). The planning, design, and use of ozone in water treatment facilities has been growing exponentially since the early 1980's (Rice, 1997). Ozonation by-products are a major concern with respect to pending regulations. Regulations and technologies are constantly changing, and the drinking water industry requires robust and flexible tools to balance microbial protection against by-product formation. Mechanistic-based models have been widely used to understand and predict coagulation, sedimentation, filtration, and membrane separation processes and aid researchers in understanding these complex processes. It is now possible to develop mechanistic-based models for ozonation by-product formation by using data collected over the last seventy-five years from atmospheric and aquatic studies of ozone reactions. However, additional knowledge of natural organic matter (NOM) reactions with key intermediates and simultaneous quantification of two oxidants present during ozonation (molecular ozone and hydroxyl radicals).

Recent regulatory activities have resulted in the development of the Microbial and Disinfection By-Product (M/DBP) cluster. The components of this cluster include the proposed Disinfectant/Disinfection By-Products (D/DBP) Rule (USEPA, 1994), the Interim Enhanced Surface Water Treatment Rule (IESWTR) and requirements to provide microbial protection. Included is a proposed regulation to set the Maximum Contaminant Level (MCL) for bromate at 10 µg/L. The MCL will be based upon a Practical Quantification Limit (PQL) using USEPA Method 300.0 (Pfaff et al., 1989; Gordon et al., 1994). Future regulations for bromate may be lowered since 10 µg/L currently represents a  $10^{-4}$  excess cancer risk level and is higher than the normal regulatory level of  $10^{-6}$  (Wilbourn, 1993; Kurokawa et al., 1992; Song et al., 1996a).

Based upon work in organic-free laboratory water and waters containing NOM, it is generally accepted that bromate formation occurs in three steps: (1) molecular ozone ( $O_3$ ) oxidizes bromide ( $Br^-$ ) to aqueous bromine ( $HOBr/OBr^-$ ); (2) hydroxyl ( $HO^\bullet$ ) radicals present during ozonation oxidize aqueous bromine to bromite ( $BrO_2^-$ ); and (3)  $O_3$  rapidly oxidizes bromite to bromate ( $BrO_3^-$ ). NOM is involved in bromate formation in several ways: (1) affects ozone demand of a water and rate of ozone decay, (2) affects  $HO^\bullet$  concentrations, (3) reacts with  $HOBr/OBr^-$ , and (4) probably reacts with brominated radicals. Two widely accepted strategies for controlling bromate formation include pH depression or ammonia addition. Our understanding has been limited as to the efficacy of these two bromate control strategies in natural waters that contain NOM, since NOM affects the mechanisms of bromate formation.

## APPROACH

The goal of this project is to develop an understanding of bromate formation and control in natural waters during ozonation. We will conduct detailed experiments with on a single water source, but the answers to key questions will be transferable to nearly all water treatment plants practicing ozonation. The single water supply will be Colorado River water (CRW) since it is a major water supply for six southwestern states, and many water treatment plants using CRW are, or will be, practicing ozonation. *The central hypothesis is that a kinetic-based understanding of NOM reactions with hydroxyl (HO) radicals and bromine (HOBr/OBr<sup>-</sup>) over a range of*

*temperatures is necessary to develop mechanistic models for bromate formation in bulk waters.* The study will address the following specific objectives:

1. Task 1 - Develop a comprehensive database of bromate concentrations, ozone residuals, and HO<sup>•</sup> radical concentrations;
2. Task 2 - Determine rates of reaction between bromine species (HOBr and OBr<sup>-</sup>) with NOM;
3. Task 3 - Calibrate and verify a bromate formation mechanistic-based model that includes DOC reactions and temperature dependency;
4. Task 4 - Simulate bromate control measures necessary to meet proposed and future MCLs under a wide range of conditions (e.g., pH depression and ammonia addition).

## **METHODS**

Laboratory kinetic batch and continuous-flow, plus pilot-scale, ozonation was conducted with a single source water (Colorado River water) to study bromate formation. Bromide, aqueous bromine (HOBr and OBr<sup>-</sup>), bromate, and ozone residual were directly measured. HO<sup>•</sup> radical concentrations were assessed indirectly through the use of a probe compound (parachlorobenzoic acid). Experiments were conducted at different initial pH, bromide, alkalinity, ammonia, and ozone dose conditions.

Additional batch experiments using bromine or chlorine, separately were also undertaken to evaluate rate constants for the reaction between these compounds and NOM. Isolated NOM was used in these studies, from the Colorado River and Suwannee River. Limited experiments were conducted using pre-ozonated NOM isolates. Experiments were conducted at different initial pH and temperature conditions.

## **RESULTS**

### **Ozonation of Colorado River Water: Ozone and Hydroxyl Radicals**

In general, effects of individual water quality parameter on O<sub>3</sub> exposure, R<sub>CT</sub> as well as HO<sup>•</sup> exposure show trends that most water quality parameters have negative impact on O<sub>3</sub> exposure except alkalinity (Table E-1). Water quality parameters such as pH, temperature and DOC have positive influence on R<sub>CT</sub> and negative impact for bromide and alkalinity. These results in the HO<sup>•</sup> exposure increase as water pH, temperature and DOC increase, but decreases as bromide and alkalinity increase.

**Table E-1 Trends of O<sub>3</sub> exposure, R<sub>CT</sub> and HO<sup>•</sup> exposure on water quality parameters during ozonation**

Parameters	Level	O <sub>3</sub> -CT	R <sub>CT</sub>	HO <sup>•</sup> -CT
pH	↑	↓	↑	↑↑
Temperature		↓	↑	↑
Bromide		↓	↓	↓↓
Alkalinity		↑	↓	↓↓
DOC		↓	↑	↑

The value of R<sub>CT</sub> is not affected by water hydraulics when applying the same water quality and ozone treatment conditions. R<sub>CT</sub> 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 O<sub>3</sub> dose to obtain the same O<sub>3</sub> residuals.) for waters with and without ammonia addition. The hydraulics seem does not affect the ratio of HO<sup>•</sup> and O<sub>3</sub> concentrations throughout the process. However, this only applies for the slow stage of ozonation. The fast stage of R<sub>CT</sub> for continuous flow ozonation cannot be determined due to unavailability of O<sub>3</sub> residual and HO<sup>•</sup> concentration profiles in the process. When water quality is changed as a result of coagulants addition, the water pH decreases and the turbidity has becomes, which representing that more particles have been removed and thus the R<sub>CT</sub> decreases. The difference of R<sub>CT</sub> in batch and pilot ozonation of water with coagulant addition is because the difference of O<sub>3</sub> residual profiles. Overall O<sub>3</sub> dose is probably key of controlling R<sub>CT</sub> since it is a function of the required O<sub>3</sub> residual, the ozone key kinetics.

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 O<sub>3</sub> and HO<sup>•</sup> concentrations were investigated. The following conclusions were withdrawn from the results:

- By adding trace amount of PCBA into water, the concentrations of HO<sup>•</sup> formation during ozonation process can be determined by the product of O<sub>3</sub> concentrations and R<sub>CT</sub>.
- Ozonation of water with a set of water quality and treatment condition, a two-stage R<sub>CT</sub> was defined, which is a fast stage followed by a slow stage.
- Fits of R<sub>CT</sub> data at variable pH results in the following regressions:  

$$R_{ct} (0-2 \text{ min}): 3E-14*(pH)^{6.5486}$$

$$R_{ct} (>2 \text{ min}): 1E-13*(pH)^{5.4762}$$
- The values of R<sub>CT</sub> are affected by water quality parameters. In general, R<sub>CT</sub> values at fast stage are higher than at slow stage by a factor of 2 to 3 and the values of R<sub>CT</sub> increases as water pH, temperature, and concentration of DOC increase and decreases as bromide and alkalinity levels decrease.

## Ozonation of Colorado River Water: Bromate Formation

Kinetics of  $O_3$  decomposition and  $HO^\bullet$  generation 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 alkalinity act positive effect on bromate formation, whereas DOC concentration and ammonia perform inverse effect on bromate formation. Chapter 4 mentioned 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. Values of  $R_{CT}$  show a linear relationship with bromate formation. In general,  $R_{CT}$  values increase as increasing levels of pH, temperature and DOC and increasing rate of bromate formation except DOC, which act as inverse impact on bromate formation (Table E-2). On the other hand,  $R_{CT}$  values decrease as increasing bromide and inorganic carbon concentrations, which resulting in increase of bromate formation. Ammonia acts as treatment that efficiently reduces bromate formation. Increasing addition of ammonia enhances reduction rate of bromate formation while still maintaining  $R_{CT}$  unchanged.

**Table E-2 Summary of relationship among the parameters,  $R_{CT}$  and bromate formation for CRW water ozonation (CRW baseline conditions:  $O_3$ : 3 mg/L;  $Br^-$ : 170 mg/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
Bromide	+	–	+
pH	+	+	+
Temperature	+	+	+
Alkalinity	+	–	+
Ammonia	+	unchanged	–
NOM	+	+	–

Experimental reactions involved in the minimization of bromate through the addition of ammonia are summarized below:

- Compared to 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 high dose of ammonia is applied.
- After 20 minutes of reaction, up to 60% and 85% of bromate reduction were achieved at pH 7.5, and 8.5, respectively when the ration of  $NH_4^+/Br^-$  is greater than 15. However, even a very high dose of ammonia is applied, some bromate still forms and additional bromate reduction is due to the reaction of ammonia with ozone which resulting in less ozone residuals remaining in waters.

- Addition of ammonia does not affect ozone decomposition due to its slow reaction with ozone and HO<sup>•</sup>, and therefore, R<sub>CT</sub> remains unchanged.
- Based upon bromate formation pathways, intermediate bromine, oxidized from bromide by O<sub>3</sub>, is inhibited by reacting with ammonia to prevent from further oxidation by O<sub>3</sub> and HO<sup>•</sup> through direct/indirect and direct pathways.
- Bromate removal by ammonia addition is not efficient if waters that have low pH and/or already contain high ammonia level. This is important for practical application when considering bromate control using ammonia in water treatment facilities. In addition, addition of ammonia probably cannot achieve bromate below MCL if waters contain high level of bromide.

### **Bromine (and Chlorine) Reactions with NOM**

Rate determination experiments were conducted with the addition of aqueous chlorine or bromine in various concentrations of different types of NOM (both unaltered and preozonated forms) under various pH and temperature conditions. 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.
- Both HOBr and OBr<sup>-</sup> (or HOCl and OCl<sup>-</sup>) appear to participate in reacting with NOM, and, however, the effect of pH as well as temperature does not significantly change the rate of reaction. Preozonated reduces mainly on oxidation reactivity of NOM, which occurs more favorable in chlorination than in bromination.
- Bromine reactions with NOM are nearly an order of magnitude faster than similar chlorine reactions.
- Bromine reaction rate constants for non-ozonated NOM were 30 to 130 M<sup>-1</sup>s<sup>-1</sup>, and 15 to 75 M<sup>-1</sup>s<sup>-1</sup> for pre-ozonated NOM. For non-ozonated NOM:  $K \text{ (M}^{-1}\text{s}^{-1}) = 34 \cdot (\text{UVA}_{254}) - 14$ .
- Chlorine reaction rate constants for non-ozonated NOM were 1 to 5 M<sup>-1</sup>s<sup>-1</sup>, and 1 to 2 M<sup>-1</sup>s<sup>-1</sup> for pre-ozonated NOM.
- Faster NOM HOBr reaction sites (μM), based upon a  $K=10^5 \text{ M}^{-1}\text{s}^{-1}$ , can be estimated by the following reaction:  $0.153(\text{UVA}_{254}) + 0.053$ . These sites are all considered to form TOBr.
- Slower NOM HOBr reaction sites have a K value of approximately 50 M<sup>-1</sup>s<sup>-1</sup>, and are of similar order of magnitude between pH 5 through 11. These sites are assumed not to produce TOBr.

### **Kinetic-Based Mechanistic Model**

A bromate formation model was evaluated that predicted bromate formation at elevated pH well. The model was less accurate in predicting the short-term formation of bromate at lower pH levels. The effect of NOM ( $K = 15 \text{ M}^{-1}\text{s}^{-1}$ ) on the reaction/consumption of HOBr and OBr<sup>-</sup> was not negligible, accounting for ~30% reduction in bromate formation (3 mg/L DOC). Modeling of carbonate radical concentrations and scavenging by NOM was considered as a means of

improving these predictions. The model was used to predict bromate formation under ozone contact conditions representative of chemical disinfection for cryptosporidium. The simulations suggest that a combination of pH depression and ammonia addition, not either one or the other techniques, would be effective in combination. Changes in pH can have issues associated with corrosion in water distribution systems. Ammonia addition offers potentially greater flexibility than acid addition, based upon changing influent bromide levels or water temperatures.

Bromate control (pH depression and ammonia addition) were simulated for theoretical ozonation scenarios. Ozone residual and  $R_{ct}$  was modeled as follows:

$$O_3 + O_3 \rightarrow 3O_2 \quad K = 2e10*[OH^-] \quad (E-1)$$

$$R_{ct} (0-2 \text{ min}): 3E-14*(pH)^{6.5486} \quad (E-2)$$

$$R_{ct} (>2 \text{ min}): 1E-13*(pH)^{5.4762} \quad (E-3)$$

Bromate formation at one ozone exposures (1E04 M-min) were compared. An ozone exposure of 1.3E-4 M-min was reported to be equivalent to 2 log inactivation of cryptosporidium (Pinkernell and von Gunten, 2001). This ozone exposure corresponds to roughly 10 minutes of contact time at pH 8.2. Simulated bromate formation between pH 7.4 and 7.8 with a range of ammonia doses is presented in Figure 7-3. At higher pH levels, increasing the ammonia to bromide molar ratios can decrease bromate formation to below the MCL of 10  $\mu\text{g/L}$ . The slopes of bromate formation as a function of pH or ammonia to bromide ratios are approximately equal, and suggests that the two strategies are equally effective.

$BrO^\bullet$  was a critical intermediate. Future research should investigate these reactions further, possibly examining chemical additives that selectively scavenge  $BrO^\bullet$ , could offer a potential strategy for bromate formation. Alternatively, probes for quantifying  $BrO^\bullet$  would be useful in order to track this important intermediate during future research.

Figure E-1 Model predictions for bromate control based upon Equations 7-10 through 7-12 (bromide = 2.12E-6M, Alkalinity = 1 mM, DOC = 3 mg/L)

