ABSTRACT

Chlorine demand from nitrite in wastewater is thought to be significant, especially when the wastewater is partially nitrified. Large and unpredicted chlorine demand makes chlorine residual control during disinfection difficult. Thus, understanding the impact of nitrite on chlorine consumption is necessary for better control of the quality of disinfection.

In this work, chlorine demand was studied in three ways. First, wastewater breakpoint curves were generated with unchlorinated secondary effluent undergoing nitrification. The slope of the rising leg of the breakpoint curves typically was less than one for samples where partial nitrification was suspected. Second, breakpoint curves were generated using pure water containing ammonia and nitrite. These breakpoint curves were similar to those obtained with field samples. Third, a kinetic model was developed to predict chlorine residuals along the breakpoint curve. Reactions between chlorine, ammonia, and nitrite were considered. The amount of nitrite, contact time, and the rate constants for nitrite reactions affected the shape of the breakpoint curve. The model successfully simulated the laboratory breakpoint curves. The nitrite concentrations of the wastewater samples were predicted by a simplified model and then the chlorine demand was predicted by the full model. Good matches were observed between the predicted chlorine demand and chlorine demand calculated from plant data.

The results from the model predictions and laboratory data show that nitrite plays a important role in the chlorination process. The effect of nitrite on the breakpoint curve is predictable. Chlorine demand from other chemical compounds be estimated by adding the appropriate reactions to the kinetic model.

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1. INTRODUCTION

Chlorine is the most widely used disinfectant in the United States and many other countries. Drinking water, wastewater, and cooling water are chlorinated for disinfection and other purposes as part of the treatment process (White, 1992).

In the chlorination process, wastewater is held for a sufficient time (called the contact time) in the chlorine contact tank until the desired microbial inactivation has been achieved. The water quality of treated water usually is evaluated based on the measured chlorine residual. The fact that chlorine and some chlorination by-products are toxic to aquatic biota has caused considerable concern over the discharge from publicly owned treatment works (POTWs). As a result, the residual chlorine entering a receiving stream is regulated and monitored.

Although chlorine is a popular disinfectant, the kinetics of chemical reactions involved in chlorination process still are not well understood. Interfering compounds such as nitrite and other inorganic ions exert a chlorine demand and reduce the efficiency of disinfection. Therefore, prediction and control of the chlorine demand reactions in the chlorination process is an important issue in water and wastewater disinfection.

The overall goal of this project was to determine the effects of a reduction in chlorine dosage on disinfection at the Buffalo Sewer Authority. A critical aspect of this overall problem is the quantification and prediction of chlorine demand. The objective of the University at Buffalo portion of the overall project was to examine the effect of chlorine demand (especially from nitrite) on wastewater chlorination by conducting bench scale water and wastewater chlorination experiments and simulate the results with mathematical models.

2. LITERATURE REVIEW

2.1 Scope

In this chapter, the chemistry of wastewater chlorination and the importance of nitrite in wastewater chlorination will be reviewed.

2.2 Chlorine Chemistry

Chlorine is the most widely used disinfectant for drinking water and wastewater in the United States. Chlorine is commonly applied in the forms of chlorine gas, sodium hypochlorite solution, or calcium hypochlorite. Chlorine gas is only slightly soluble in the water (solubility = 1.88×10^{-3} at 20°C; Lide and Frederikse, 1995). Once it is dissolved in water, hydrolysis occurs rapidly:

$$Cl_2 + H_2O = HOCl + H^+ + Cl^- \qquad (2\text{-}1)$$

Nearly complete hydrolysis occurs in a few tenths of a second at room temperature (Gordon *et al.*, 1987). Sodium and calcium hypochlorite also hydrolyze to form hypochlorous acid. Hypochlorous acid is a weak acid ($pK_a = 7.54$ at 25°C, Morris, 1966). It partially dissociates to form hypochlorite ion (OCl^-) as follows:

$$HOCl = H^+ + OCl^- \qquad (2\text{-}2)$$

In waters at pH 6.5 to 8.5, both species are presented to some degree. The sum of HOCl and OCl^- concentrations is called free available chlorine or FAC.

2.3 Breakpoint Phenomenon

2.3.1 Ammonia-chlorine Breakpoint Curves

Without ammonia or nitrogenous organics present, the chlorination of water would be very simple. The total chlorine always would be equal to the free available chlorine. However, ammonia and/or organic nitrogen exists in many waters. Chlorine reacts with ammonia and some nitrogenous organics to form a class of compounds called chloramines. Chloramines are characterized by the presence of one or more N-Cl bonds. Three types of chloramines can be formed from the reactions of chlorine and ammonia nitrogen:

$$HOCl + NH_3 = NH_2Cl \text{ (monochloramine)} + H_2O \qquad (2\text{-}3)$$

$$HOCl + NH_2Cl = NHCl_2 \text{ (dichloramine)} + H_2O \qquad (2\text{-}4)$$

$$HOCl + NHCl_2 = NCl_3 \text{ (trichloramine)} + H_2O \qquad (2\text{-}5)$$

The competition between reactions depends on the pH of the water, temperature, contact time, and most important of all, the initial chlorine to ammonia ratio (White, 1992). Monochloramine and dichloramine are the two dominant species in most cases. Chlorine reacts with some nitrogenous organics analogously to equation 2-3 or 2-4 to form organic chloramines. The sum of all chloramines is called combined available chlorine or CAC. The sum of the CAC and FAC is called total residual chlorine (TRC).

The breakpoint curve represents graphically the relationship between the residual chlorine and the added chlorine (chlorine dose). A theoretical breakpoint curve is shown in Figure 2-1. In this curve, several characteristic zones can be identified. The dominant reaction in zone 1 is the reaction between chlorine and ammonia indicated in equation 2-3.

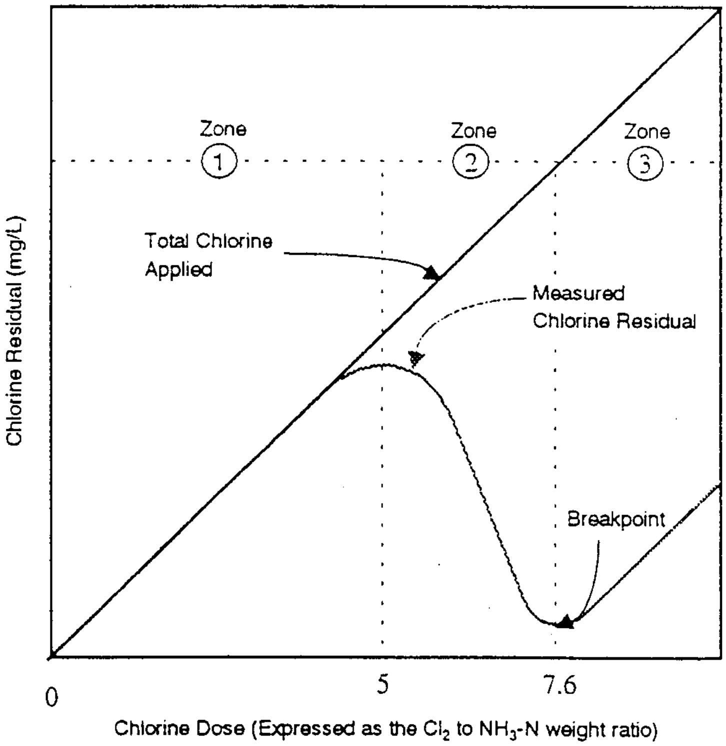

Figure 2-1: Theoretical Breakpoint Curve

The chlorine residual contains mainly monochloramine. The total chlorine maximum occurs theoretically at a chlorine to ammonia ratio of 5:1 by weight (molar ratio of 1:1). As the chlorine to ammonia molar ratio starts to exceed 1:1, the reaction in equation 2-4 starts and forms dichloramine. (Dichloramine also can be formed from the disproportionation of monochloramine: $NH_2Cl + NH_2Cl = NHCl_2 + NH_3$) Dichloramine is unstable. Reactions contribute to the breakdown of chloramines to nitrogen gas are listed in Section 3.

The dose at which ammonia has been oxidized completely and the residual chlorine is minimized is called the breakpoint. The theoretical chlorine to ammonia weight ratio at the breakpoint is 7.6. At this point, most chloramines are oxidized, and a very low chlorine residual remains in the water.

The dominant residual existing in the water in zone 3 is free chlorine. Only small amount of dichloramine and trichloramine can be found. An increase in the chlorine dose in this zone results in a corresponding increase in the free available chlorine.

2.3.2 Chlorine Demand

Chlorine demand is defined as the difference between the amount of chlorine added to the water (chlorine dose) and the amount of chlorine remaining (chlorine residual) at the end of a specific contact time. Inorganic ions (Fe^{2+}, Mn^{2+}, H_2S, CN^-, NO_2^- and others) in the water react with chlorine rapidly, causing a rapid initial chlorine demand. The most common reactions and the amount of chlorine consumed by these ions are listed in Table 2-1.

Table 2-1 Chlorine Demand from Inorganic Ions (adapted from White, 1992)

Ion	Reactions with Chlorine	Demand (mg Cl_2 demand/mg ion)
Fe^{2+}	$2\ Fe^{2+} + HOCl + 5\ H_2O - 2\ Fe(OH)_3(s) + 5\ H^+ + Cl^-$	0.64
Mn^{2+}	$Mn^{2+} + HOCl + H_2O - MnO_2(s) + 3\ H^+ + Cl^-$	1.3
HS^-	$HS^- + HOCl - S(s) + H_2O + Cl^-$	2.2 (HS^- as S)
	$HS^- + 4\ HOCl - SO_4^{2-} + 5\ H^+ + 4\ Cl^-$	8.8 (HS^- as S)
NO_2^-	$NO_2^- + HOCl - NO_3^- + H^+ + Cl^-$	5 (NO_2^- as N)
CN^-	$CN^- + HOCl - CNO^- + H^+ + Cl^-$	2.73
	$2\ CN^- + 5\ HOCl + H_2O - N_2(g) + 2\ HCO_3^- + 5\ Cl^- + 5\ H^+$	6.82

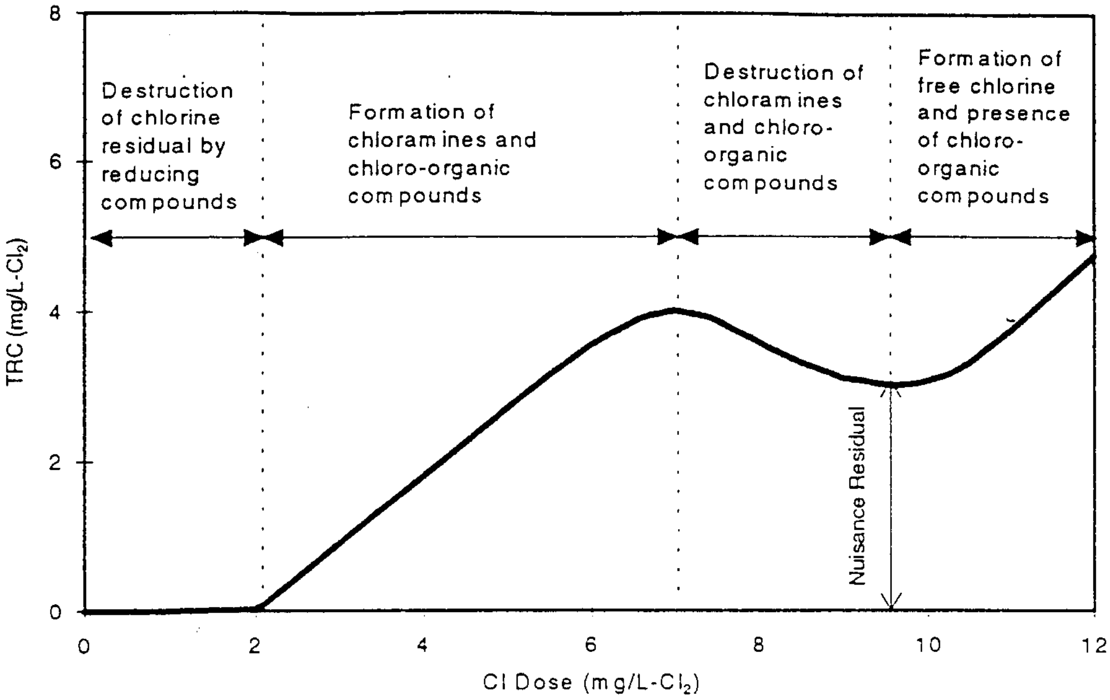

Figure 2-2: Breakpoint Curve of Water Containing Chlorine Demand

The theoretical ammonia breakpoint curve usually does not occur in wastewater treatment plants. Two major factors that affect the breakpoint curve in wastewater are chlorine demand and organic nitrogen (Burton *et al.*, 1991; White, 1992; Gordon, 1987). When chlorine is added to wastewater, as shown in Figure 2-2, some readily oxidized substances (such as Fe^{2+}, Mn^{2+}, HS^-, NO_2^- and organic matter) react with chlorine rapidly, reducing the chlorine residual. After meeting this immediate demand, the chlorine continues to react with ammonia as discussed previously.

2.3.3 Effects of Organic Nitrogen

Organic nitrogen consists of mainly proteinaceous compounds and their hydrolysis products, such as peptides and amino acids. It is difficult to predict the reactivity of organic nitrogen compounds because of their complexity and variety. Proteins are a constituent of plant and animal life in aquatic environment and are found in both animal and human waste. Proteins are composed of elements (such as nitrogen, carbon, and sulfur) which exert a chlorine demand. Organic nitrogen typically reacts with chlorine at a much slower rate than does ammonia. Taras

(1953) studied the consumption of chlorine by both ammonia and organic nitrogen. He found that the ammonia nitrogen reacted completely after one hour of contact time, while the simple, unsubstituted amino nitrogen of many amino acids was consumed within several hours. Protein nitrogen showed only a trace loss even after many days.

The disinfection potency of active chlorine species decreases in the order: chlorine gas > hypochlorous acid > hypochlorite > dichloramine > monochloramine > organic chloramine (Feng, 1966). Feng (1966) showed that the presence of a small amount of organic nitrogen significantly decreased the effectiveness of the residual chlorine without changing the amount of the residual appreciably. Scully and coworkers (1996) studied wastewater disinfection in brewery waste that contained significant amount of organic nitrogen. They found that waters with high total organic nitrogen to NH_3 ratio (>1.5) were poorly disinfected by aqueous chlorine. However, if preformed monochloramine was used, a much faster rate of disinfection was reached.

It was found that waters containing both ammonia and organic nitrogen do not exhibit near zero chlorine residual at the breakpoint (White, 1992). The unreducible residual at the breakpoint is called the nuisance residual because it has little disinfection ability (see Fig. 2-2).

2.4 Nitrification and Denitrification of Wastewater

2.4.1 Nitrification

Nitrification refers to the biological oxidation of the reduced nitrogen (primarily ammonia) to nitrate. Nitrifying organisms are present in almost every aerobic biological treatment process, but usually their biological activity is limited. Nitrification processes can be classified based on the degree of separation of the BOD removal and the nitrification functions. Both processes can occur in a single reactor ("single-stage" process) or the carbon oxidation and nitrification can be performed in separate reactors (Burton *et al.*, 1991). The nitrifying ability, which can be quantified as the fraction of nitrifying organisms in the wastewater, has been correlated with the BOD_5/total Kjeldahl nitrogen (BOD_5/TKN) ratio. It has been found that when the BOD_5/TKN ratio is greater than about 5, the process is usually classified as combined carbon oxidation and nitrification process. When this ratio is less than 3, the process is a separate-stage nitrification process (US EPA, 1975).

Nitrification is an autotrophic process in which nitrifiers use carbon dioxide rather than organic carbon as the carbon source. Two steps are involved in the nitrification process. In the first step, the bacteria *Nitrosomonas* convert ammonia nitrogen to nitrite. Subsequently, *Nitrobacter* bacteria oxidize nitrite to nitrate. The stoichiometry for the reactions occurring in nitrification is listed below (Painter, 1970; US EPA, 1975):

$$\begin{aligned}&55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- -\\&\qquad C_5H_7O_2N + 54\ NO_2^- + 57\ H_2O + 104\ H_2CO_3\end{aligned}\tag{2-6}$$

(Often abbreviated as: $NH_4^+ + 1.5\ O_2 \xrightarrow{Nitrosomonas} NO_2^- + 2\ H^+ + H_2O$)

$$\begin{aligned}&400\ NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- + 195\ O_2 -\\&\qquad C_5H_7O_2N + 3\ H_2O + 400\ NO_3^-\end{aligned}\tag{2-7}$$

(Often abbreviated as: $NO_2^- + 0.5\ O_2 \xrightarrow{Nitrobacter} NO_3^-$)

2.4.2 Denitrification

The nitrate nitrogen in wastewater can be converted to nitrogen gas under anoxic conditions. This process is called denitrification. Several genera of bacteria are involved in this process, including *Achromobacter, Aerobacter, Alcaligenes, Bacillus, Brevibacterium, Flavobacterium, Lactobacillus, Micrococcus, Proteus, Pseudomonas*, and *Spirillum* (Burton *et al.*, 1991). Different from nitrifying organisms, these bacteria are called facultative heterotrophic because they are able to use either nitrate or oxygen as the terminal electron acceptors. This explains why an anoxic environment, in which no electron acceptors such as oxygen competes with nitrate, is required to achieve denitrification. Two steps are included in this process. The first step is the conversion of nitrate to nitrite, called nitrate dissimilation (eqn. 2-8). Nitrite produced in the second step is converted sequentially to nitric oxide, nitrous oxide, and finally nitrogen gas ($NO_3^- - NO_2^- - NO - N_2O - N_2$) (eqn. 2-9). This two-step process is called dissimilation. The last three compounds are gases and are readily released to the atmosphere. An external carbon source is needed as an electron donor in the denitrification process. Methanol is the most commonly used carbon source in the United States. If methanol is used as the electron donor and nitrate as the acceptor, denitrification can be represented as a two-step process as shown in equations 2-8 and 2-9:

$$NO_3^- + ⅓\ CH_3OH - NO_2^- + ⅓\ H_2O + ⅓\ H_2CO_3\tag{2-8}$$

$$NO_2^- + ½\ CH_3OH + ½\ H_2CO_3 - ½\ N_2 + HCO_3^- + H_2O\tag{2-9}$$

2.4.3 Partial Nitrification

Classical nitrification theory says that the rate of nitrification is controlled by the conversion of ammonia to nitrite. Consequently, nitrite concentrations remain very low (US EPA, 1975). High nitrite concentrations occur occasionally in activated sludge plant effluents (Anthonisen *et al.*, 1976; Halmo and Eimhjelle, 1981). Few treatment plants measure nitrite and nitrate concentrations separately. Detection of nitrite usually occurs indirectly in secondary effluents through a large increase in the chlorine requirement in disinfection process. Biological nitrification can be inhibited by chemical and environmental factors, such as toxicity (e.g. excess ammonia), low dissolved oxygen, low temperature, low alkalinity, non-optimum pH, and an operating MCRT that is low for the environmental conditions (Randall and Buth, 1984; Anthonisen *et al.*, 1976; Quinlan, 1986; Wild *et al.*, 1971; Rols *et al.*, 1994). Randall and Buth (1984) found that temperature influenced nitrate formation more than nitrite formation. This allows for a critical temperature range of about 10°C to17°C in which nitrite formation is slower than nitrite disappearance and a nitrite build-up can be observed (Randall and Buth, 1984; Rols *et al.*, 1994).

2.5 The Role of Nitrite in Wastewater Chlorination

In wastewater chlorination, nitrite can exert a chlorine demand by reacting with both free chlorine and monochloramine. As shown in Table 2-1, one mg/L of nitrite nitrogen consumes five mg/L of chlorine as Cl_2. The reaction of nitrite and chlorine is a multistep process. The mechanisms were given by Cachaza and coworkers (1976) as listed below:

$$HOCl + NO_2^- = NO_2Cl + OH^- \tag{2-10}$$

$$NO_2Cl + NO_2^- = N_2O_4 + Cl^- \tag{2-11}$$

$$N_2O_4 + OH^- - NO_3^- + NO_2^- + H^+ \tag{2-12}$$

$$NO_2Cl = NO_2^+ + Cl^- \tag{2-13}$$

$$NO_2^+ + OH^- - NO_3^- + H^+ \tag{2-14}$$

As listed above, the oxidation of nitrite does not start with the oxygen atom transfer but proceeds by Cl^+ transfer from HOCl to NO_2^- to give NO_2Cl (nitryl chloride) as a reduction intermediate (eqn. 2-10). Nitryl chloride then reacts with a second nitrite ion to form N_2O_4 (eqn. 2-11) or dissociates into the very reactive nitronium ion (NO_2^+) (eqn. 2-13). The oxidation of nitrite by monochloramine is similar. The overall reaction is:

$$NH_2Cl + NO_2^- + H_2O \rightarrow NH_4^+ + NO_3^- + Cl^- \qquad (2\text{-}15)$$

Margerum *et al.* (1994) proposed an acid-assisted mechanism for the reaction of nitrite with monochloramine to form nitryl chloride:

$$H^+ + NH_2Cl + NO_2^- = NH_3 + NO_2Cl \qquad (2\text{-}16)$$

2.6 Research Needs

In the chlorine/nitrite reactions, nitrite reacts much faster with free chlorine (rate constant is 24600 $mM^{-1}min^{-1}$ at pH 7, Johnson and Margerum, 1991) than with monochloramine (rate constant is 0.215 $mM^{-1}min^{-1}$, Margerum *et al.*, 1994). However, the reaction of free chlorine with ammonia to form monochloramine is faster (rate constant is 2.5×10^5 $mM^{-1}min^{-1}$, Morris and Isaac, 1983) than the chlorine demand reactions with nitrite. Therefore, it is anticipated that monochloramine will form and react with nitrite during the chlorination process. The quantitative effect of chlorine demand from nitrite on water chlorination is still unknown. There is a need to understand the effect of nitrite on breakpoint curves which will allow practitioners to calculate the amount of chlorine consumed in the water chlorination process and to have a better control over the effluent water quality.

3. METHODS

This chapter describes the experimental approach, materials, analytical procedures, and mathematical model employed throughout this research. Experiments in this research were conducted in the Environmental Engineering Research Laboratories at the State University of New York at Buffalo.

3.1 Approach

Breakpoint curves were obtained by conducting water chlorination experiments on deionized water containing phosphate and spiked with ammonium-N and nitrite. In addition, breakpoint curves also were conducted on Buffalo Sewer Authority (BSA) wastewater during nitrification and non-nitrification periods to observe nitrite's role during water chlorination. Sodium hypochlorite was used as the chlorine source. A chlorine stock was made from 4 ~ 6 percent sodium hypochlorite (NaOCl) solution (Fisher Scientific, Inc.). Phosphate buffer (added to 0.1 M total phosphate) was added to every water and wastewater sample before chlorination to maintain a pH of 7 during chlorination. A chlorine contact time of 30 minutes was used for wastewater samples collected from March 29, 1996 to June 11, 1996. Fifteen minutes of contact time was used for samples from June 18, 1996 to December 19, 1996 and all the pure water samples. All samples were kept in the dark during chlorination to prevent photolysis.

3.2 Materials

Water used in all laboratory experiments were deionized water supplied by a Barnsted Nanopure system (Barnsted Company, Dubuque, Iowa). In all cases, reagent or higher-graded chemicals were used. Glassware used in this work was soaked in 10% nitric acid, rinsed with deionized water, and then dried. Glassware was tested to be free of measurable chlorine demand.

3.3 Analytical Procedures

3.3.1 Sample Collection

Wastewater samples were collected from the Buffalo Sewer Authority's Bird Island Wastewater Treatment Plant on an approximately weekly basis. A simplified flow schematic of the plant is shown in Figure 3-1. Samples were collected from a manhole connecting the effluent of final clarifiers to the chlorine contact tank.

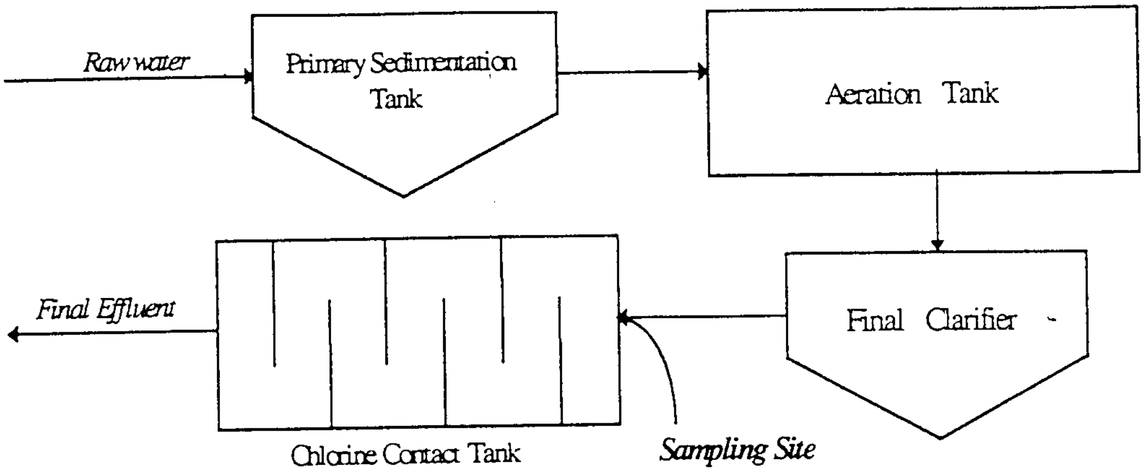

Figure 3-1 Schematic of BSA Wastewater Treatment Plant and the Sampling Site

3.3.2 pH

The pH and ammonium-nitrogen were measured within 6 hours of wastewater sample collection before phosphate buffer was added. The pH was measured by an Expandable Ionanalyzer from Orion Research Inc.

3.3.3 Ammonium-nitrogen

The phenate method (APHA *et al.*, 1992) was used to measure the ammonium-nitrogen. Fresh ammonium chloride standards were prepared for every ammonium-nitrogen analysis. Absorbances in this research were measured with a diode array spectrophotometer from Hewlett-Packard Company (Model 8452A).

3.3.4 Chlorine

Chlorine stock solutions were standardized by amperometric titration method (APHA *et al.*, 1992). Chlorine residuals, including free chlorine, monochloramine, and dichloramine, were measured by amperometric titration using a Model 397 Amperometric Cl Titrimeter from Fisher Scientific, Inc.

3.4 Kinetic Model

A kinetic model was developed to simulate the breakpoint curve for water containing ammonium and chlorine demand. The chemical reactions and rate constants used in this model are presented in Table 3-1. The model takes into account the formation and hydrolysis of monochloramine and dichloramine (reactions 1-6), free chlorine and monochloramine demand (reactions 11 and 12), and other breakpoint reactions (reactions 7-10 and 14-16). Rate constants for most of the reactions in Table 3-1 were used by Jafvert and Valentine (1992) to describe the breakpoint chlorination of ammonia without demand. The rate constants for reaction 15 and 16 were determined by Jafvert and Valentine by fitting their model to data.

Rate expressions for changes in the concentrations of $HOCl$, NH_3, NH_2Cl, $NHCl_2$, NCl_3, NOH, and NO_2^- were constructed for the reactions in Table 3-1. A computer program was written in Visual Basic to calculate species concentrations over time. Differential equations were solved using the fourth-order Range-Kutta-Fehlberg algorithm. Inputs to the model were chlorine dose range, initial ammonia, initial nitrite, pH, total phosphate, and algorithm convergence parameters. The program calculates species concentration at a user-supplied chlorine contact time across the breakpoint curve.

Table 3-1 Kinetic Model Equations[1]

Reaction	Rate Constant	Reference
1. $HOCl + NH_3 - NH_2Cl + H_2O$	$2.5e5\ mM^{-1}min^{-1}$	Morris and Isaac, 1983
2. $NH_2Cl + H_2O - HOCl + NH_3$	$1.27e\text{-}3\ min^{-1}$	Morris and Isaac, 1983
3. $HOCl + NH_2Cl - NHCl_2 + H_2O$	$21\ mM^{-1}min^{-1}$	Morris and Isaac, 1983
4. $NHCl_2 + H_2O - HOCl + NH_2Cl$	$3.83e\text{-}5\ min^{-1}$	Margerum *et al.*, 1978
5. $NH_2Cl + NH_2Cl - NHCl_2 + NH_3$ [2]	$1.42e\text{-}3\ mM^{-1}min^{-1}$	Valentine and Jafvert, 1988
6. $NHCl_2 + NH_3 - NH_2Cl + NH_2Cl$ [3]	$3.6e\text{-}4\ mM^{-1}min^{-1}$	Hand and Margerum, 1983
7. $NH_2Cl + NHCl_2$ - Products [4]	$9.17e\text{-}4\ mM^{-1}min^{-1}$	Jafvert and Valentine, 1992
8. $NHCl_2 + H_2O - NOH$ + Products [5]	$9.7e\text{-}4\ min^{-1}$	Jafvert and Valentine, 1987

Table 3-1 Continued

Reaction	Rate Constant	Reference
9. $NOH + NHCl_2$ - $HOCl$ + Products	1.67e3 $mM^{-1}min^{-1}$	Jafvert and Valentine, 1992
10. $NOH + NH_2Cl$ - Products	5.0e2 $mM^{-1}min^{-1}$	Jafvert and Valentine, 1992
11. $HOCl + NO_2^-$ - $NO_3^- + Cl^- + H^+$	8.32e4 $mM^{-1}min^{-1}$	Johnson and Margerum, 1991
12. $NH_2Cl + NO_2^- + H_2O$ - $NO_3^- + NH_4^+ + Cl^-$ [6]	2.15e-1 $mM^{-1}min^{-1}$	Margerum *et al.*, 1994
13. $HOCl + NHCl_2$ - $NCl_3 + H_2O$ [7]	56.56 $mM^{-1}min^{-1}$	Hand and Margerum, 1983
14. $NHCl_2 + NCl_3 + 2H_2O$ - $2HOCl$ + Products [8]	3.33e2 $mM^{-1}min^{-1}$	Hand and Margerum, 1983
15. $NH_2Cl + NCl_3 + H_2O$ - $HOCl$ + Products [9]	8.33 $mM^{-1}min^{-1}$	Jafvert and Valentine, 1992
16. $NHCl_2 + 2HOCl + H_2O$ - $NO_3^- + 5H^+ + 4Cl^-$	13.83 $mM^{-1}min^{-1}$	Jafvert and Valentine, 1992

Notes:
1. Rate constants for Eqn. 5, 6, 8, and 12-15 were adjusted to pH 7 and a total phosphate of 0.1 M.
2. $k = 4.17\text{x}10^{-1}\,[H^+] + 2.17\text{x}10^{-5}\,[H_2PO_4^-] + 5.33\text{x}10^{-2}\,[H_3PO_4]$ ($mM^{-1}min^{-1}$)
3. Rate = $k\,[NHCl_2][NH_3][H^+]$
4. Products may include N_2, H_2O, Cl^-, H^+, NO_3^-, and unidentified reaction products.
5. Rate = $k\,[NHCl_2][OH^-]$
6. $k = 4.56\text{x}10^{2}\,[H^+] + 2.76\text{x}10^{-3}\,[H_2PO_4^-]$ ($mM^{-1}min^{-1}$)
7. $k = 9.53\text{x}10^{-1}\,[HPO_4^{2-}] + 5.4\,[OCl^-] + 1.97\text{x}10^{5}\,[OH^-]$ ($mM^{-1}min^{-1}$)
8. Rate = $k\,[NHCl_2][NCl_3][OH^-]$
9. Rate = $k\,[NH_2Cl][NCl_3][OH^-]$

4. RESULTS

4.1 Introduction

The results of the experiments conducted throughout this research will be presented in this chapter. Breakpoint chlorination was conducted on wastewater samples collected at BSA from March 1996 to December 1996. Representative breakpoint curves and results from chlorine demand studies will be presented in this chapter. Breakpoint curves conducted on pure water spiked with ammonia and/or nitrite also will be presented in this chapter.

4.2 Wastewater Characterization and Chlorination

4.2.1 Wastewater Characterization

For each wastewater sample collected, pH and ammonia were measured. In addition, plant data were collected including temperature, chlorine dose, and chlorine demand. The pH values of wastewater samples are shown in Figure 4-1. The pH values ranged from 7.20 to 7.96 with an average pH of 7.52. Ammonium concentrations in the samples are plotted in Figure 4-2. Note the dramatic drop in the concentration of ammonium in the samples collected after June 4, 1996. This indicates the occurrence of nitrification in the aeration tanks. Figures 4-3 and 4-4 show the chlorine demand and temperature of the wastewater. Chlorine demand was calculated by subtracting the residual measured on site from the daily chlorine dose. Four negative chlorine demand values in over three hundred samples are assumed to result from measurement errors and have no significance. Note that the small increase in the chlorine demand when the temperature was increasing from around 10°C to 17°C in the late spring. At the same time, the ammonium concentration dropped dramatically. Chlorine demand increased again up to seven times higher than normal when the temperature decreased back to about 10°C in the early winter.

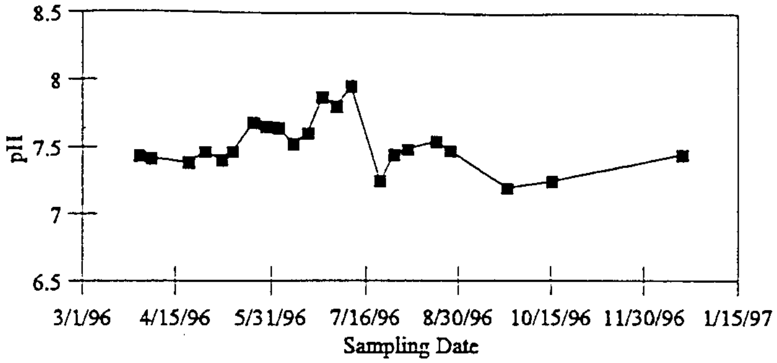

Figure 4-1: Wastewater pH

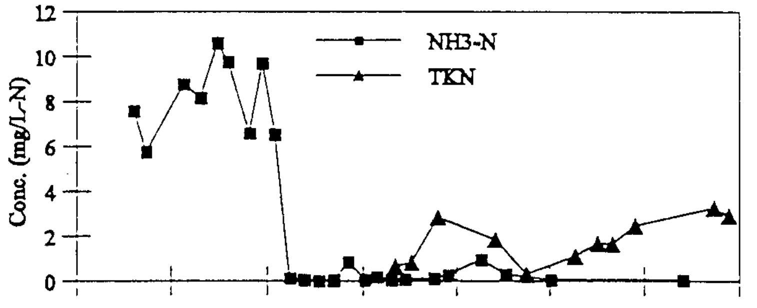

Figure 4-2: Wastewater Ammonia and TKN Concentration

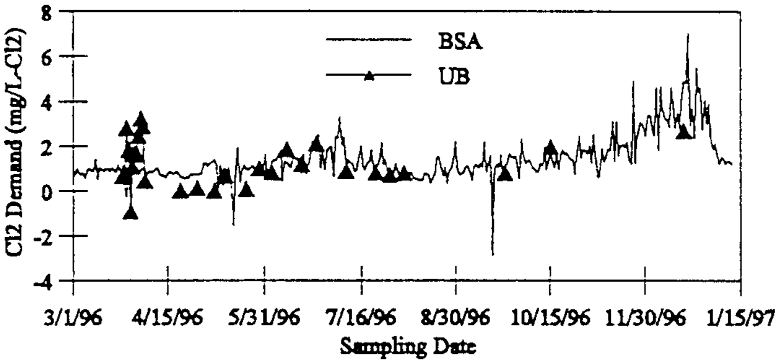

Figure 4-3: Wastewater Chlorine Demand

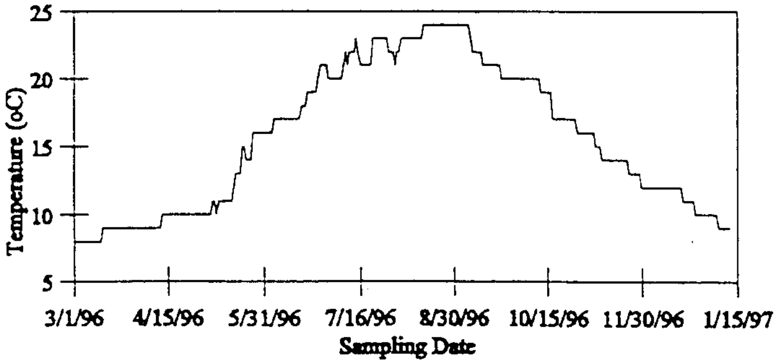

Figure 4-3: Temperature of Wastewater

4.2.2 Wastewater Chlorination

Over twenty breakpoint curves were conducted on the wastewater samples collected from the BSA. Two distinct types of breakpoint curves were observed. Examples of both types are shown in Figure 4-5 and all breakpoint curves are plotted in Appendix A. The first type of breakpoint curves resembles breakpoint curves on ammonia (see Figure 4-5). Type 1 curves were observed on samples collected from March 29 to June 4, 1996. The samples had an average ammonium concentration of 6.14 mg/L-N. The second type of curves were observed on samples collected after June 4, 1996 during apparent nitrification events. Type 2 curves exhibited reduced slopes in the initial portion of the breakpoint curves. The doses where the maximum TRC and breakpoints occurred were much higher than those suggested by the low ammonium levels in these samples (average NH_3-N = 0.29 mg/L).

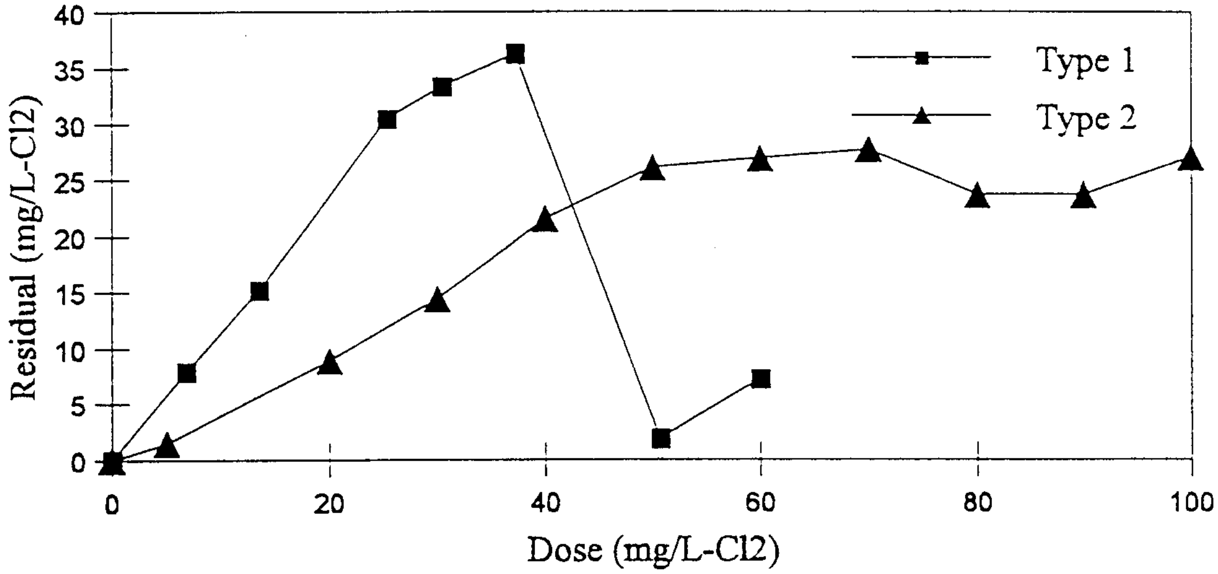

Figure 4-5: Breakpoint Curves for Wastewater from BSA
(contact time = 30 min. Type 1 sample was collected on 3/29/96, NH_3-N = 6.59 mg/L and Type 2 sample collected on 6/11/96, NH_3-N = 0.15 mg/L)

4.3 Chlorine Demand Studies

4.3.1 Effect of Nitrite Concentration

To examine how chlorine demand changes the shape of breakpoint curves, two sets of pure water chlorination experiments were conducted. The first set used an ammonium concentration of 5 mg/L-N, similar to the BSA samples collected prior to 6/4/96. The second set used a smaller ammonia concentration (0.2 mg/L-N), representing the typical unchlorinated secondary effluent at BSA during nitrification. A contact time of 15 minutes was used for all pure water samples.

The results show that a significant and measurable amount of demand was caused by nitrite during chlorination. Breakpoint curves in pure water containing 5 mg/L-N ammonia and 0, 1, or 5 mg/L-N of nitrite are shown in Figure 4-6. Note that the shift of the TRC maximum and breakpoint to higher doses increased with increasing nitrite concentration. The slope of the leading leg of the breakpoint curve decreased with increasing nitrite, while the value of the maximum TRC appeared constant. The shift in the maximum TRC and breakpoint doses were approximately equal to the chlorine equivalent of the nitrite added to the water (i.e., 5 mg/L-Cl_2 for 1 mg/L-N of nitrite and 25 mg/L-Cl_2 for 5 mg/L-N NO_2^-).

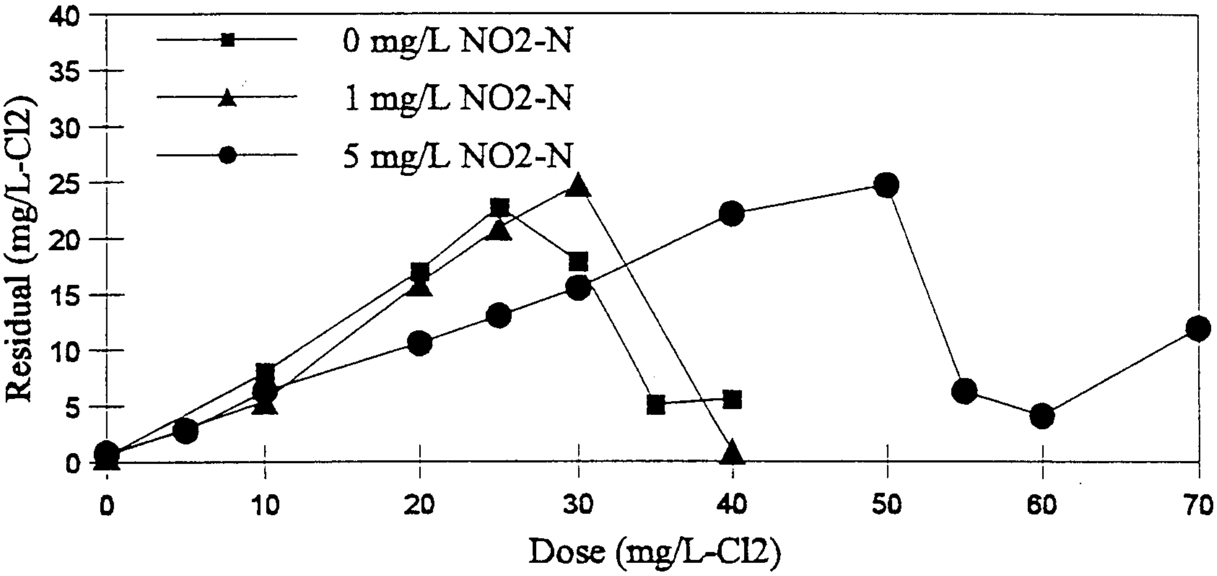

Figure 4-6: Effect of Nitrite on Breakpoint Curves - 5 mg/L-N Ammonia

Breakpoint curves for water containing 0.2 mg/L-N of ammonia are shown in Figure 4-7. The breakpoint curve for water containing 0.2 mg/L NO_2^--N shifted to the right compared to the water containing ammonia only. For the 1 and 10 mg/L-N NO_2^- curves, no TRC maximum or breakpoint was seen at the chlorine doses employed. When the nitrite concentration was 10 mg/L-N, the slope of the rising leg of the breakpoint curve was almost zero.

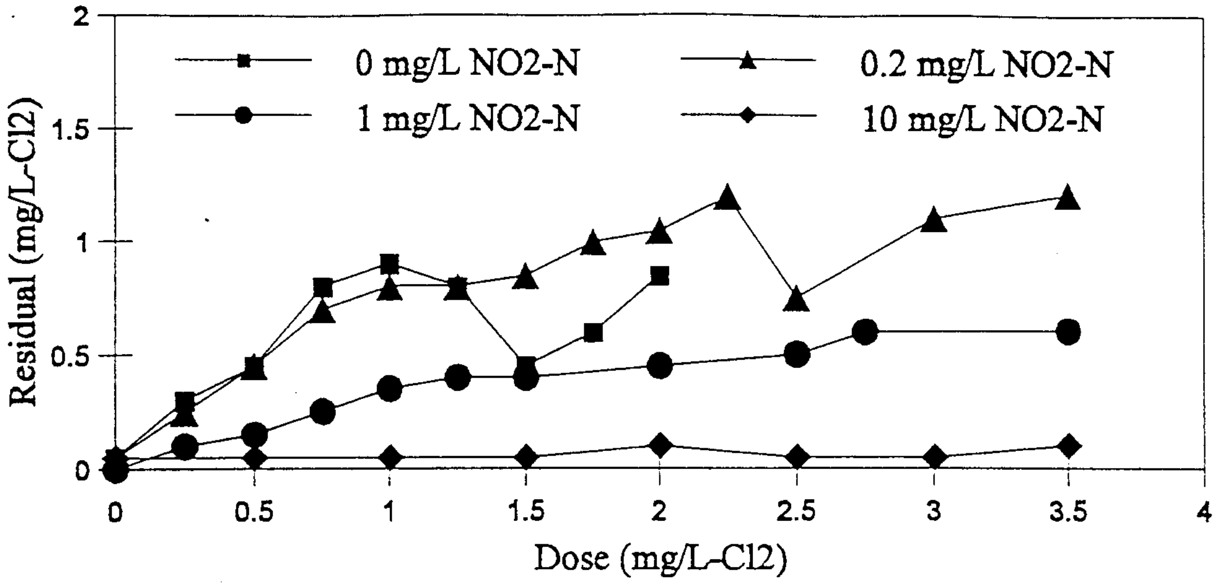

Figure 4-7 Effect of Nitrite on Breakpoint Curves - 0.2 mg/L-N Ammonia

4.3.2 Effect of Contact Time

The commonly used contact time for chlorination at BSA is 15 to 30 minutes, a time period during which neither the nitrite-monochloramine reaction nor the breakpoint reactions are complete. Therefore, contact time may influence the degree of demand reflected in breakpoint curves. Figure 4-8 shows the effect of contact time on breakpoint curves with ammonia solutions containing no other demand. Only slight differences were observed between curves. However, for the water containing 1 mg/L of nitrite-N, as shown in Figure 4-9, contact time played a bigger role. Although the total chorine maximum was relatively insensitive to contact time, the slope of the rising leg of the breakpoint curve decreased strongly with increasing contact time. The residual at the breakpoint also slightly decreased as the contact time increased.

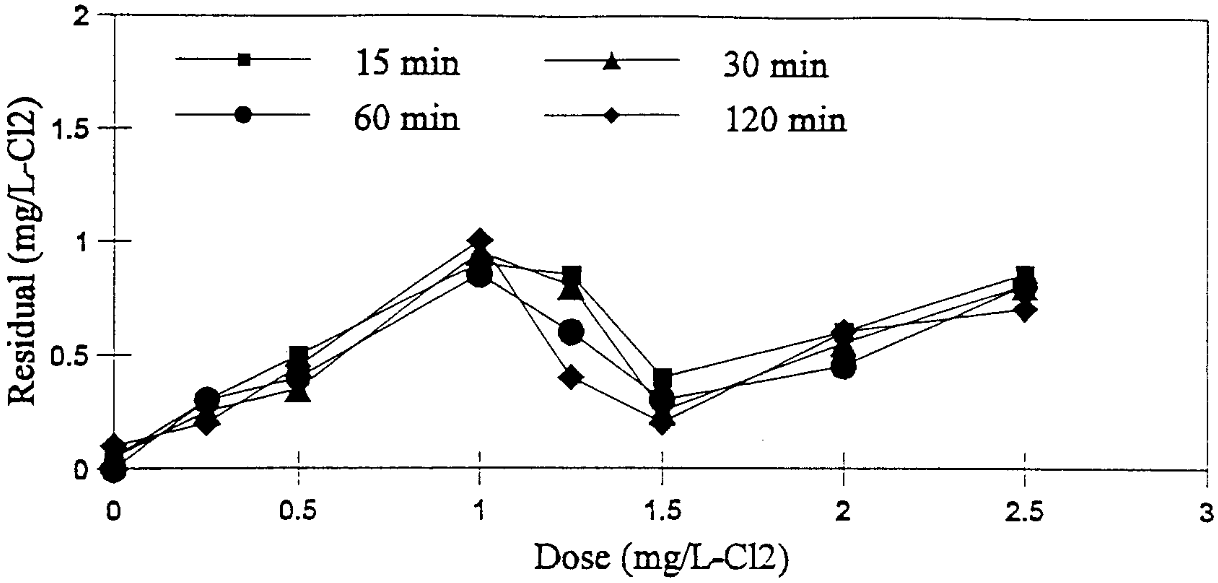

Figure 4-8: Breakpoint Curves at Various Contact Times (0.2 mg/L NH_3-N)

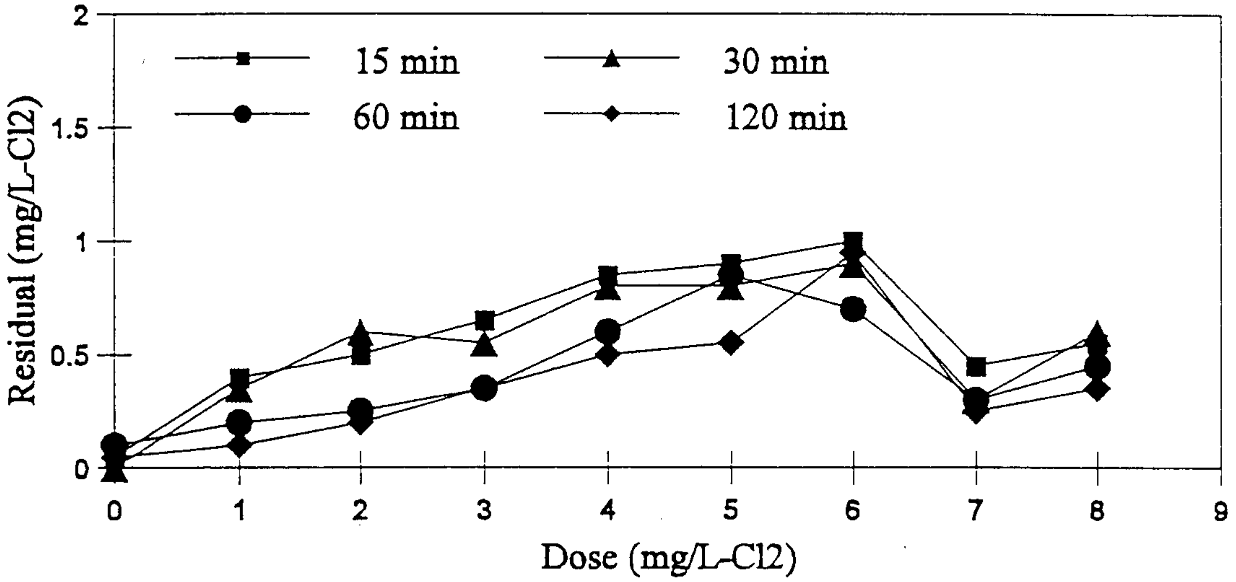

Figure 4-9: Breakpoint Curves at Various Contact Times with Demand (0.2 mg/L NH_3-N, 1 mg/L NO_2-N)

5. DISCUSSION

Comparison of experimental and simulated data for the chlorine demand studies will be presented in this chapter. Factors affecting the breakpoint curve, such as nitrite concentration, contact time, and demand reaction rate constant also will be discussed.

5.1 Effect of Nitrite on Breakpoint Curves

5.1.1 High Ammonia

For water containing 5 mg/L of ammonia nitrogen and various amounts of nitrite, model simulation and laboratory results are presented in Figures 5-1 to 5-3. In these figures, the maximum TRC and the residuals at the breakpoint remained the same for water with or without nitrite. This makes sense, since the total chlorine maximum should be equal to the initial ammonia concentration, which was constant. The chlorine doses at the TRC maximum and breakpoint shifted to higher values for waters containing nitrite. The shift of approximately five times the nitrite weight concentration was equal to the demand listed in Table 2-1.

Note that complete destruction of chlorine residual in the beginning of the breakpoint curves, as described by the traditional chlorine demand theory (Figure 2-2), did not happen. Rather, the slope of the rising leg of the breakpoint curve decreased as the nitrite concentration increased. Experimental data and model simulations compared well for the first part of the breakpoint curves. Near the breakpoint, a larger difference was noted between the data and model. This may due to the incomplete knowledge about the breakpoint reactions. As discussed in Chapter 3, the rate constants for the formation and destruction of trichloramine were not determined from experimental data but fitted to a kinetic model by Valentine *et al.* (1988). The reactions involved near the breakpoint are still poorly understood.

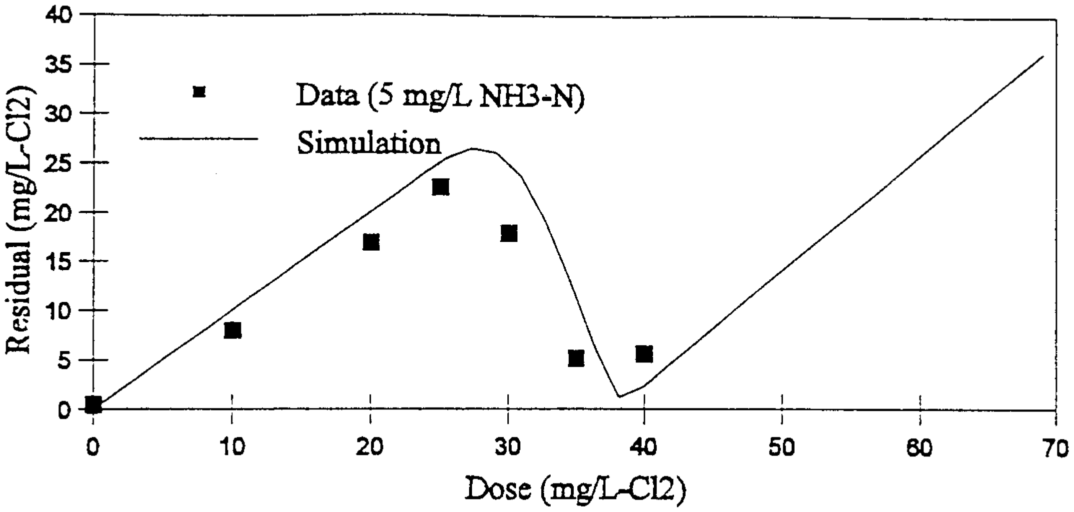

Figure 5-1: Experimental and Simulated Breakpoint Curves (0 mg/L NO_2^-N)

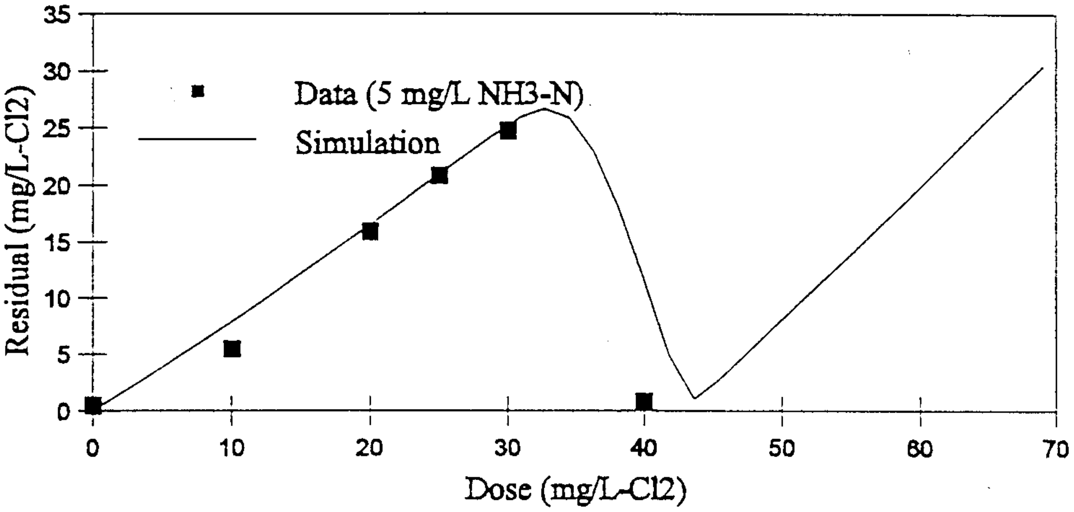

Figure 5-2: Experimental and Simulated Breakpoint Curves (1 mg/L NO_2–N)

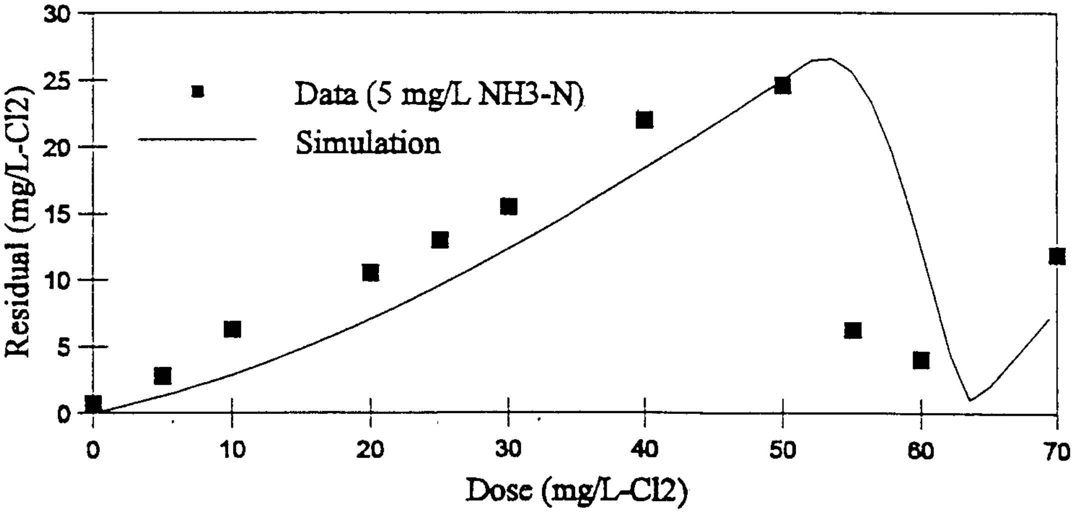

Figure 5-3: Experimental and Simulated Breakpoint Curves (5 mg/L NO_2–N)

Figures 5-1 to 5-3 show only the TRC data and model simulations. Individual chlorine species for experimental and simulated data are plotted in Appendix B. The model simulations for individual species are not as close to the data as the TRC simulations. Simulated data showed higher monochloramine values but lower dichloramine values than the experimental data. Analytical difficulty is suspected one of the reasons for this discrepancy. First, amperometric titration method measures chlorine species in the order of free chlorine, monochloramine, and then dichloramine. Different pH conditions and iodide concentrations are employed to differentiate chlorine species. Any free chlorine which is not titrated completely in the free chlorine fraction will be measured as monochloramine. Similarly, monochloramine can breakthrough into the dichloramine fraction. Thus, measured monochloramine values may be low and measured dichloramine values may be high, as observed in Appendix B.

Second, undertitration is more common when measuring high concentration solutions. The titration end point can be misjudged due to the sluggish movement of the indicator needle. This may explain why disagreement between the data and model predictions was greater in the high concentration breakpoint curves.

Third, trichloramine cannot be differentiated easily from other chlorine species in amperometric titration. It may be measured as FAC, monochloramine, or dichloramine. Therefore, the high dichloramine values measured close to the TRC maximum may occur if trichloramine was measured mostly as dichloramine.

5.1.2 Low Ammonia

Results of laboratory breakpoint curves and model simulations for low ammonia water (0.2 mg/L-N) are shown in Figure 5-4. Nitrite has a similar influence on the breakpoint curves as the shown previously in Figures 5-1 to 5-3. Note that the curvature in the rising leg is more pronounced with lower ammonia (Figure 5-4) than with high ammonia (Figure 5-3). If the nitrite dose is high enough (e.g., 10 mg/L-N), almost complete chlorine destruction can be achieved. The model also successfully simulated this case.

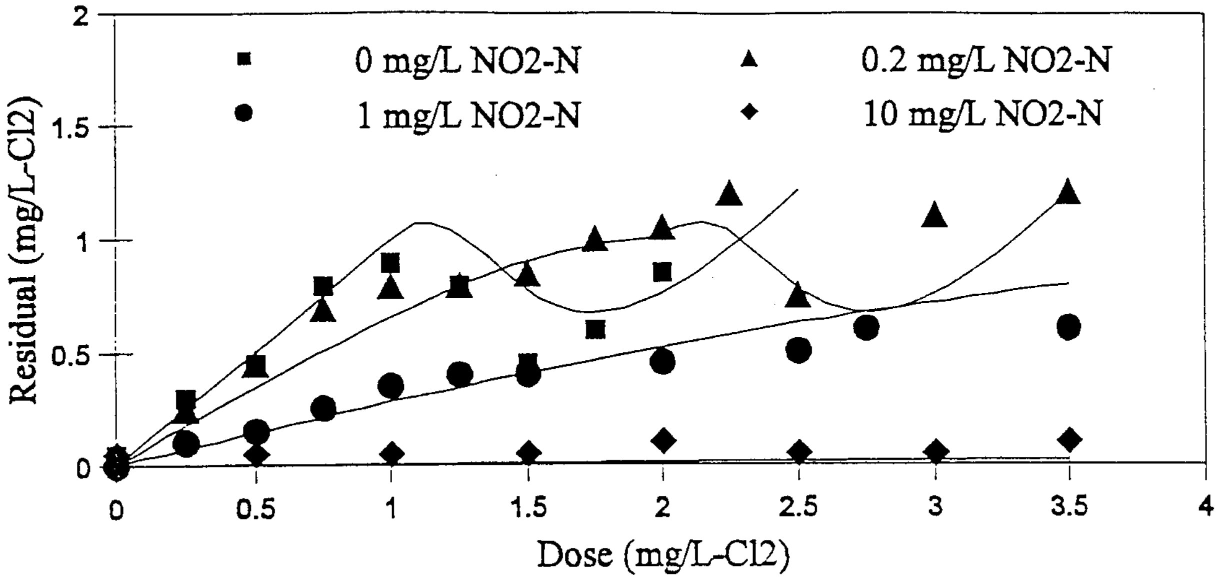

Figure 5-4: Experimental and Simulated Breakpoint Curves (0.2 mg/L NH_3–N)

5.1.3 Effect of Contact Time on Breakpoint Curves

A comparison between the simulated and laboratory data for water chlorination with different contact times is shown in Figures 5-5 and 5-6. Figure 5-5 shows the breakpoint curves for water contain no chlorine demand but ammonia. The first part of the breakpoint curve remains the same for different contact times. Both experimental data and model simulations showed that residuals at the breakpoint decreased as the contact time increased. These observations make sense, since the initial reaction to form monochloramine is much faster than the breakpoint reactions (see Table 3-1). Again, model simulations do not match experimental data near the breakpoint.

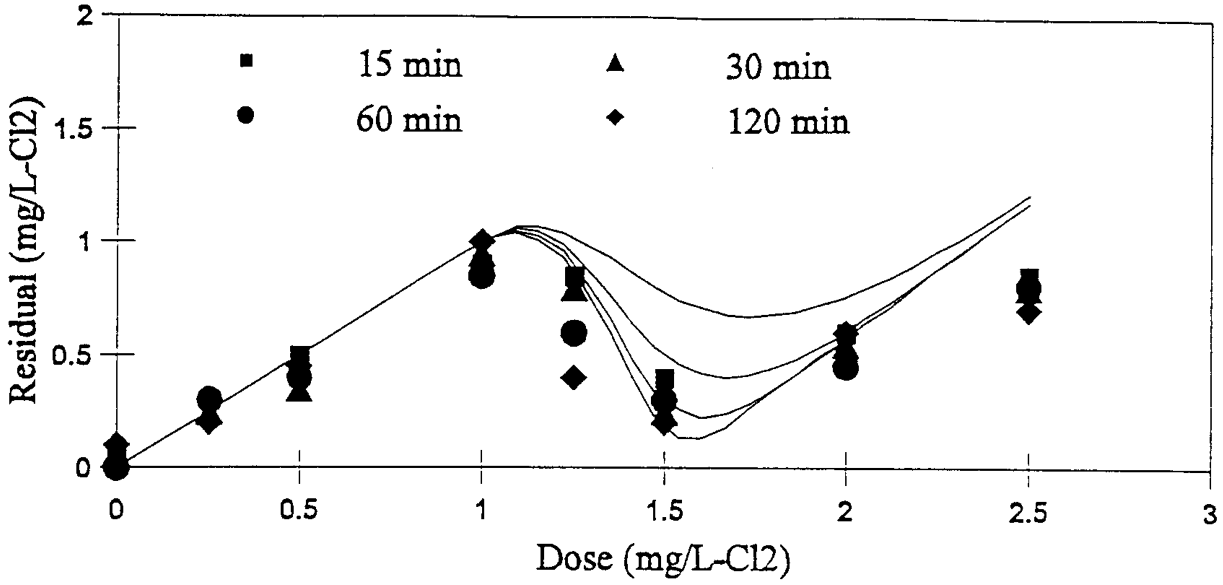

Figure 5-5: Effect of Contact Time on Breakpoint Curves (0.2 mg/L NH_3-N)

Figure 5-6 illustrates the breakpoint curves at different contact times for water containing both ammonia (0.2 mg/L-N) and 1 mg/L of nitrite-nitrogen. The shape of the first part of the curves changes as the contact time changes. Shorter contact times (e.g., 15 min) result in concave curves, while longer times (e.g., 120 min) result in convex curves.

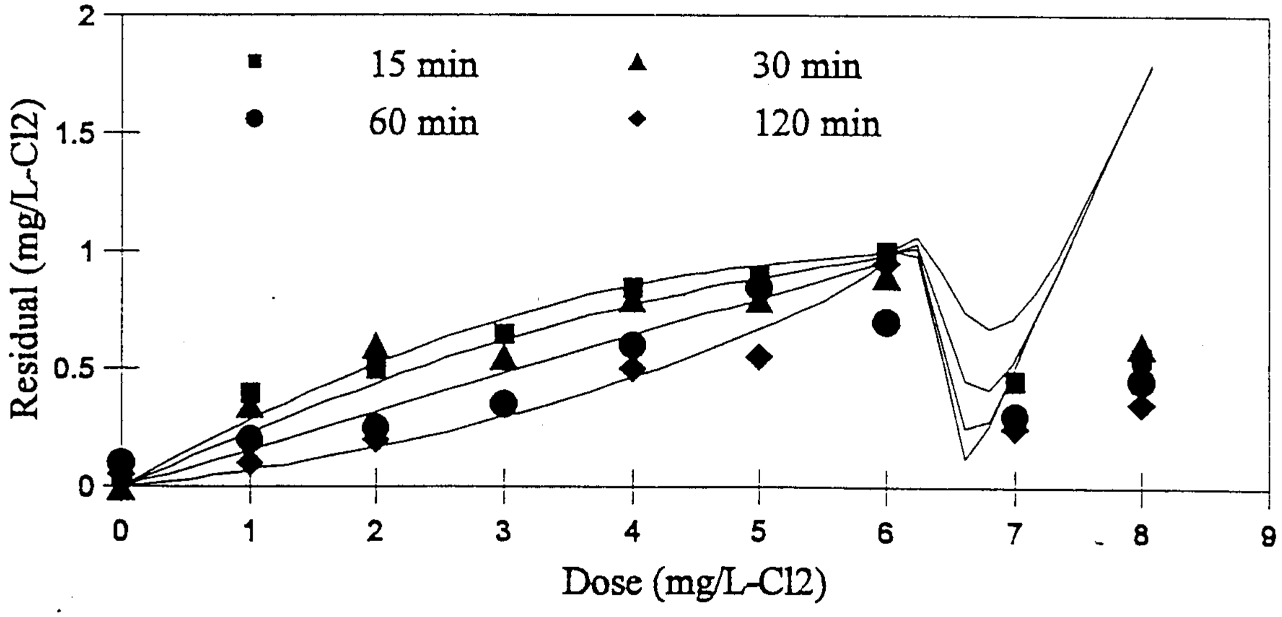

Figure 5-6: Effect of Contact Time on Breakpoint Curves (0.2 mg/L NH_3-N, 1 mg/L NO_2^--N)

Figure 5-7 shows only the simulations for the same water as mentioned above but more contact times were simulated. It shows that at longer contact times, a stronger effect is seen in the beginning of the curve. In other words, more chlorine is destroyed at longer contact times. In addition, at long contact time (i.e., 1200 minutes in Figure 5-7), the beginning of the breakpoint curve has a slope of zero. If the part of the curve with slope zero is cut off from the curve, the rest of the curve would resemble the breakpoint curve of ammonia solutions. The entire breakpoint curve will be similar to the conventional view as shown in Figure 2-2.

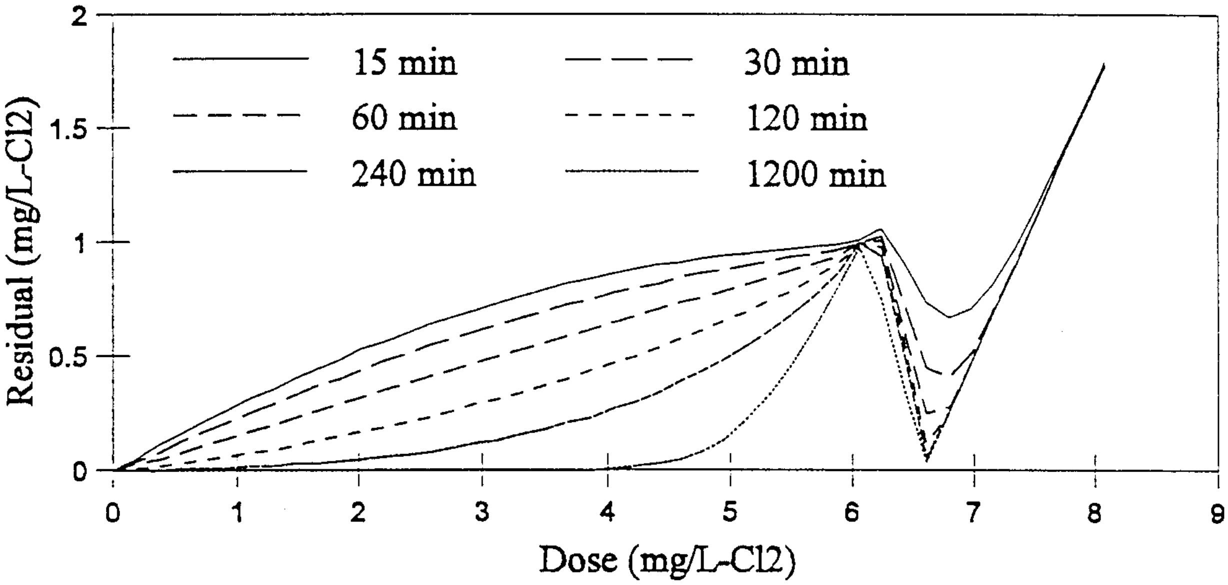

Figure 5-7: Effect of Contact Time on Breakpoint Curves (1 mg/L NO_2^--N)

On the other hand, for an extremely short contact time such as one minute, monochloramine will form but little of it will react with nitrite. TRC will increase gradually until most of the ammonia has reacted. The rest of the chlorine added will react with nitrite to remain a constant TRC to the TRC maximum.

5.1.4 Summary of the Effects for Chlorine Demand on the Breakpoint Curve

From the results presented, it is expected that the slope of the rising leg of the breakpoint curve will decrease from one to zero as the chlorine demand increases. Chlorine demand will increase as the initial demand concentration, contact time, and/or demand rate constants are increased.

Table 5-1 Rate Constants of Chlorine Demand Reactions[1]

Reactants	k ($mM^{-1}min^{-1}$)	References
$HOCl + SO_3^{2-}$	4.56e7	Folgeman *et al.*, 1989
$NH_2Cl + SO_3^{2-}$	3.44e2	Yiin *et al.*, 1987
$HOCl + CN^-$	7.32e7	Gerritsen and Margerum, 1990
$NH_2Cl + CN^-$	1.17e-3	Schurter *et al.*, 1995
$HOCl + I^-$	8.40e6	Kumar *et al.*, 1986
$NH_2Cl + I^-$	1.44e2	Kumar *et al.*, 1986
$HOCl + NO_2^-$	8.32e4	Johnson and Margerum, 1991
$NH_2Cl + NO_2^-$	2.15e-1	Margerum *et al.*, 1994

Note: 1. At pH 7 and total phosphate = 0.1 M

The effect of initial nitrite concentration is shown in Figure 5-4. Note the decrease in slope to zero with increasing initial nitrite concentration. The effect of contact time is shown in Figure 5-7. Again, the slope decreases to zero at long contact times. The rate constants of chlorine demand compounds are listed in Table 5-1. Except for the reactions of cyanide, there is a similar ratio between the rate constant with free chlorine and the rate constant with monochloramine (rate = 5.83×10^4 to 3.87×10^5). Therefore, the ratio of the demand rate constants with nitrite was used (= 3.87×10^5). Ten and one-hundredth times the nitrite rate constants were chosen to simulate the effect of demand rate constants. The results are shown in Figure 5-8. The effect of large rate constant is similar to long contact time for the rising leg of the breakpoint curve. Since the same contact time (15 minutes) was used, the chlorine residual near the breakpoint stays the same for different rate constants.

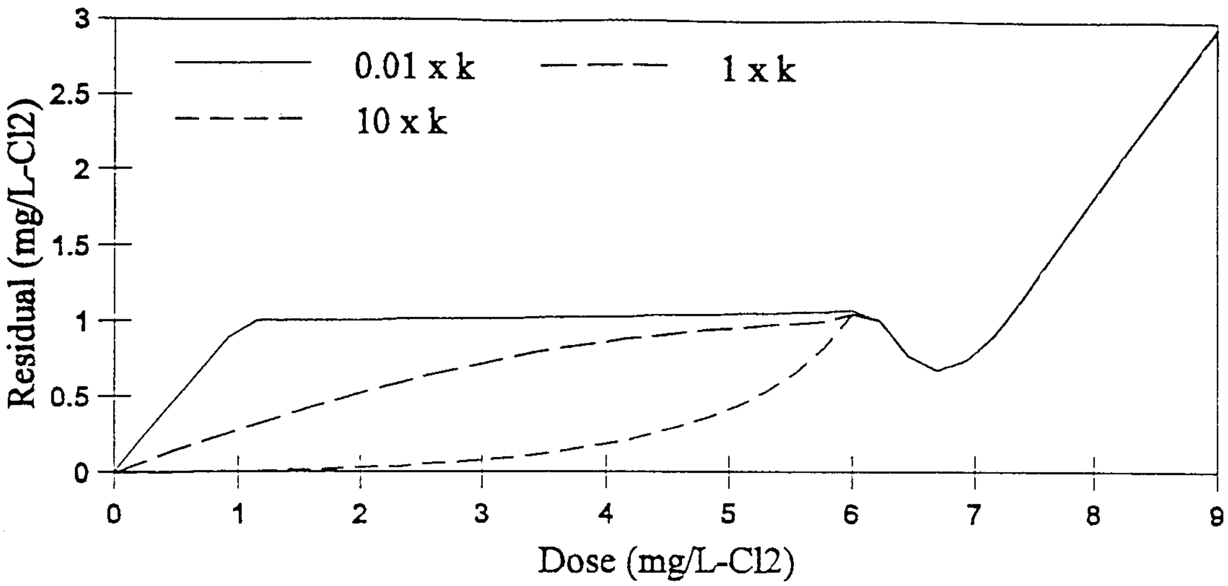

Figure 5-8: Effect of Demand Reaction Rate Constants on Breakpoint Curves

Haas and Karra (1984) proposed a two-phase chlorine demand model to describe the kinetics of chlorine demand exertion. This model assumes parallel decay of two components of total residual chlorine. One component is the fast demand which has an average rate constant of about 1.0 min^{-1}. The other component is the slow demand which has as average rate constant of about 0.002 min^{-1}, consistent with chloramine hydrolysis. This concept resembles the two demand reactions (free chlorine and monochloramine reactions) listed in Table 5-1. Both approaches have a nearly constant ratio between the fast (free chlorine) and the slow (monochloramine) demand reaction rate constants. Although the values of this ratio are different (about 500 for Haas's data, 10^5 for Table 5-1), the approach of dividing chlorine demand reactions into two or more groups may be a more realistic way to model chlorine demand kinetics.

5.2 Effect of Nitrite on Nitrified Wastewater

5.2.1 Simulation with the Full Model

The nitrite concentration was measured only in the BSA sample collected on December 19, 1996. The simulation and experimental breakpoint curves for this sample are plotted in Figure 5-9. This sample contained 0.04 mg/L of NH_3-N and 0.16 mg/L-N NO_2^-. The simulation underpredicts the TRC before the total chlorine maximum. However, agreement between the model and data is fairly good, considering the model has no adjustable parameters.

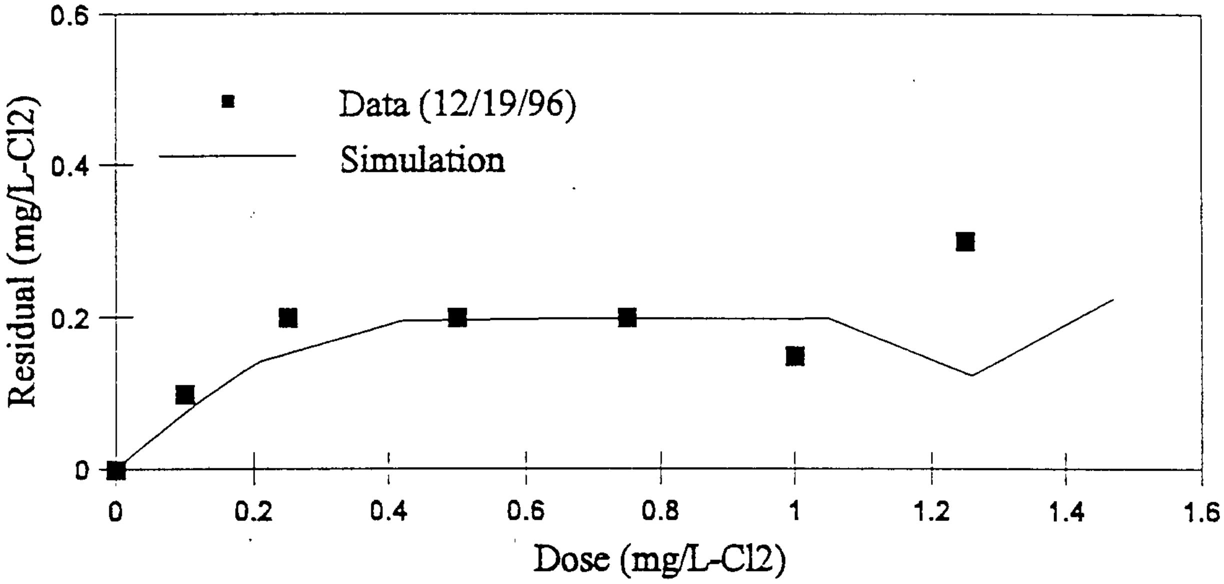

Figure 5-9: Breakpoint Curve on Wastewater Sample from BSA (12/19/96)

5.2.2 Estimation of the Nitrite Concentration

When chlorine is added to the system containing ammonia and nitrite, competition for free chlorine by ammonia and nitrite occurs. Since the rate constant of the former reaction (2.5x 10^5 mM^{-1} min^{-1}) is larger than the rate constant of the latter (8.32×10^4 mM^{-1} min^{-1}), it is assumed that most free chlorine reacts with ammonia to form monochloramine. Nitrite, then, destroys chlorine residual by reacting with monochloramine (rate constant = $2.15\text{x}10^{-1}$ mM^{-1} min^{-1}). Therefore, for the chlorine dose ranging within the rising leg of the breakpoint curve, monochloramine is destroyed throughout the contact time. A simplified model was developed based on monochloramine formation, free chlorine destruction, and monochloramine destruction by nitrite (reactions 1, 11, and 12 in Table 3-1). The development of the simplified model is shown in

Appendix C.

The simplified model was validated in three ways. First, the simplified model was used to calculate the initial nitrite concentrations using simulated chlorine residuals from the full model. Initial nitrite concentrations were calculated using Excel's solver function to minimize the sum of the squares of the errors between the simulated data and simplified model productions for given ammonia concentrations and contact times. Only simulated TRC data up to the total chlorine maximum was used. The predicted nitrite concentrations from the simplified model agreed very well with the nitrite concentrations and used in the full model simulations ($r^2 = 0.9997$). Second, the simplified model was used to predict the initial nitrite concentrations for experiments with nitrite in pure water. Predicted nitrite concentrations agreed fairly well with known initial nitrite levels ($r^2 = 0.8718$).

Third, the nitrite concentration in the wastewater samples was estimated using the simplified model. The nitrite concentration was determined by Excel's solver function by minimizing the sum of the squares of the errors between the model prediction and the chlorine residual measured for the rising leg of the breakpoint curves. Subsequently, the chlorine demand at the dose used in the plant was estimated by the full model. The relationship between the predicted demand, the actual demand (plant demand), and the demand from the experimental breakpoint curves are plotted in Figure 5-10. The predicted demand fits the BSA demand well ($r^2 = 0.92$ if the last data point is ignored). Some experimental demand values are lower than the plant demand values. An insufficient number of data points in the experimental breakpoint curves may be the reason for this discrepancy. This approach demonstrates that it is possible to predict chlorine demand from experimental breakpoint curves.

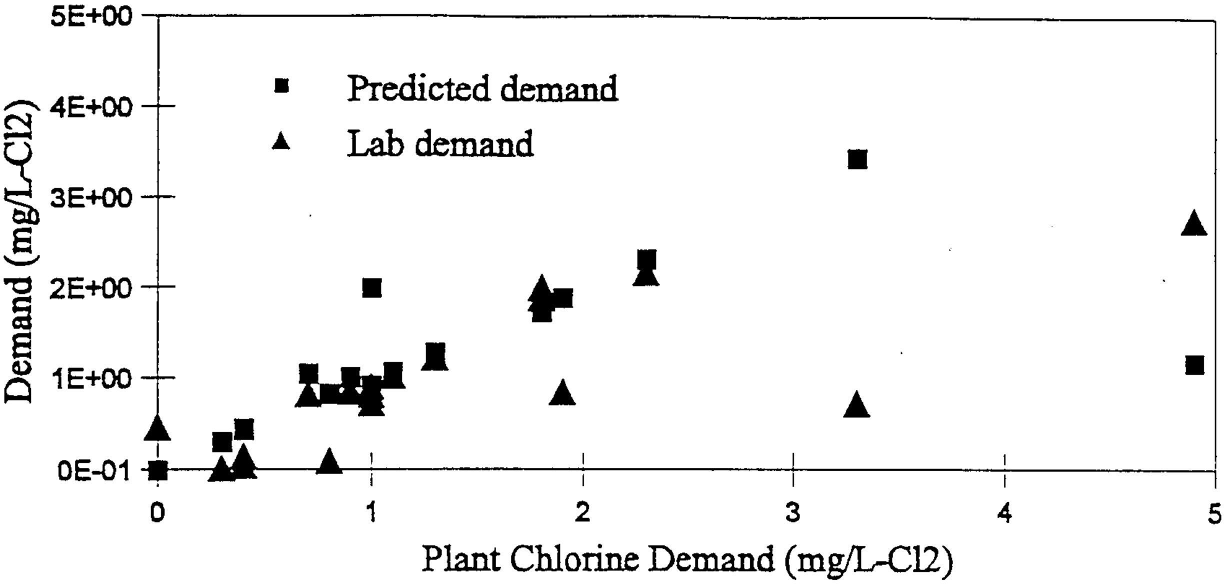

Figure 5-10: Comparison of the Chlorine Demands

6. CONCLUSIONS AND RECOMMENDATIONS

Based on this work, the following conclusions and recommendations can be made:

6.1 Conclusions

1. The effect of nitrite on breakpoint curves was modeled. Model simulations compared well with experimental data in pure systems.

2. Factors affecting breakpoint curves of water containing nitrite and ammonia include contact time and initial nitrite concentration.

3. Nitrite increases the dose required for the TRC maximum, but not the TRC maximum itself. At higher initial nitrite concentrations, the increased chlorine demand decreases the slope of the rising leg of the breakpoint curve.

6.2 Recommendations

1. More study should be done to understand the kinetics of reactions occurring at the breakpoint.

2. Simulations for other chlorine demanding compounds should be done.

3. New techniques are needed to measure trichloramine in water samples and to improve the accuracy of chlorine species measurement.

4. More chlorine demanding species should be added into the model to summarize the effects of more than one source of chlorine demand.

5. A typical rate constant, combining the effect of all chlorine demands for certain kind of wastewater without knowing the rate constants of every individual chlorine demand reaction, should be developed.

6. More work should be done to identify and differentiate the fast and the slow chlorine demands.

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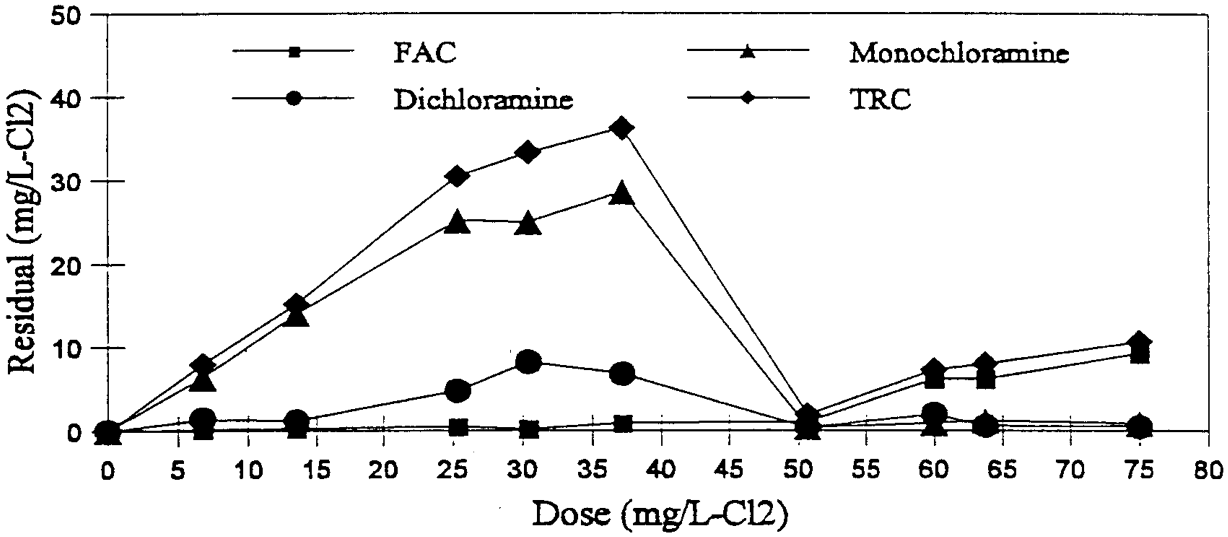
APPENDIX A: BSA BREAKPOINT CURVES

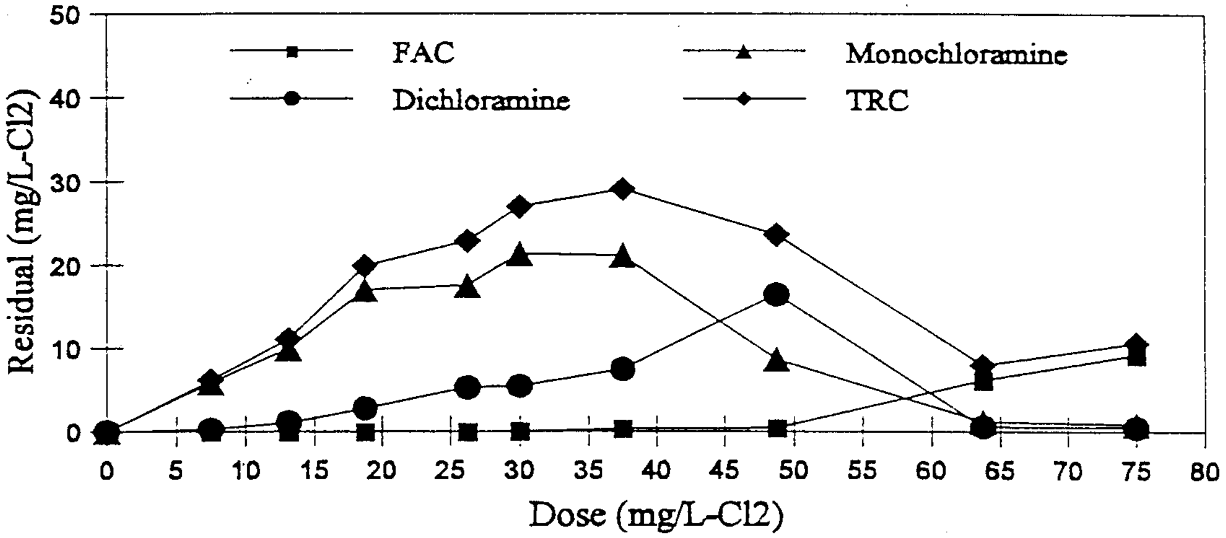
March 29, 1996 (6.59 mg/L NH_3-N, pH 7.44, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.00	0.00	0.00	0.00	0.00
6.76	8.00	0.20	6.40	1.40
13.51	15.20	0.30	14.00	1.20
25.34	30.50	0.50	25.20	4.80
30.41	33.40	0.20	25.00	8.20
37.16	36.30	0.90	28.60	6.80
50.68	1.90	1.10	0.40	0.40
60.00	7.30	6.20	0.90	2.00



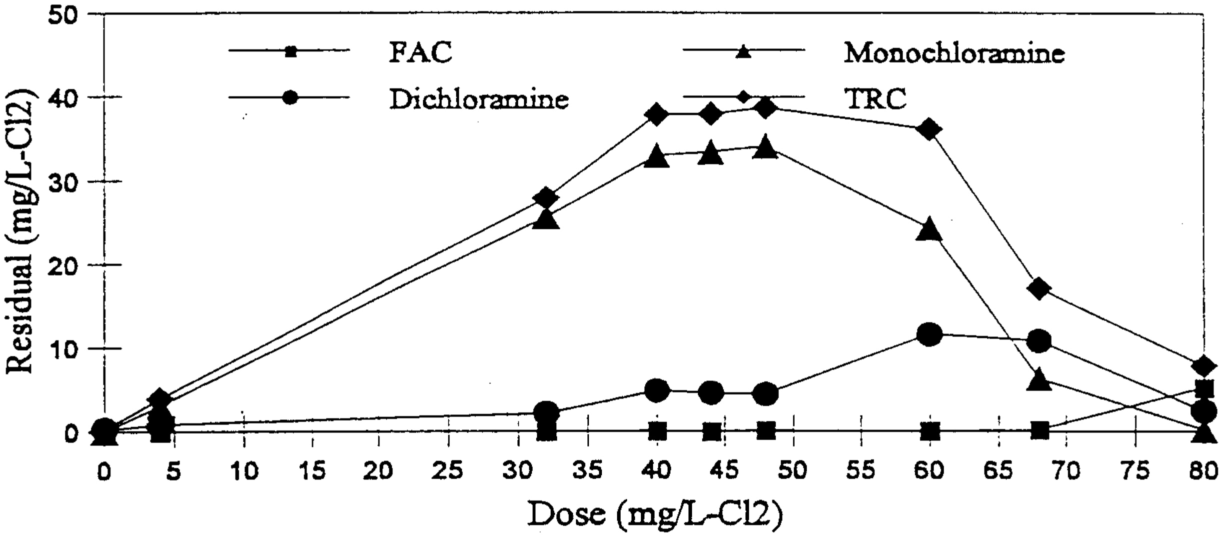
April 5, 1996 (5.77 mg/L NH_3-N, pH 7.42, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.00	0.00	0.00	0.00	0.00
7.50	6.20	0.00	5.90	0.30
13.13	11.10	0.00	10.00	1.10
18.75	19.90	0.00	17.10	2.80
26.25	22.90	0.00	17.60	5.30
30.00	27.00	0.10	21.40	5.50
37.50	29.10	0.40	21.20	7.50
48.75	23.65	0.45	8.70	16.50
63.75	8.00	6.20	1.20	0.60
75.00	10.60	9.20	0.90	0.50



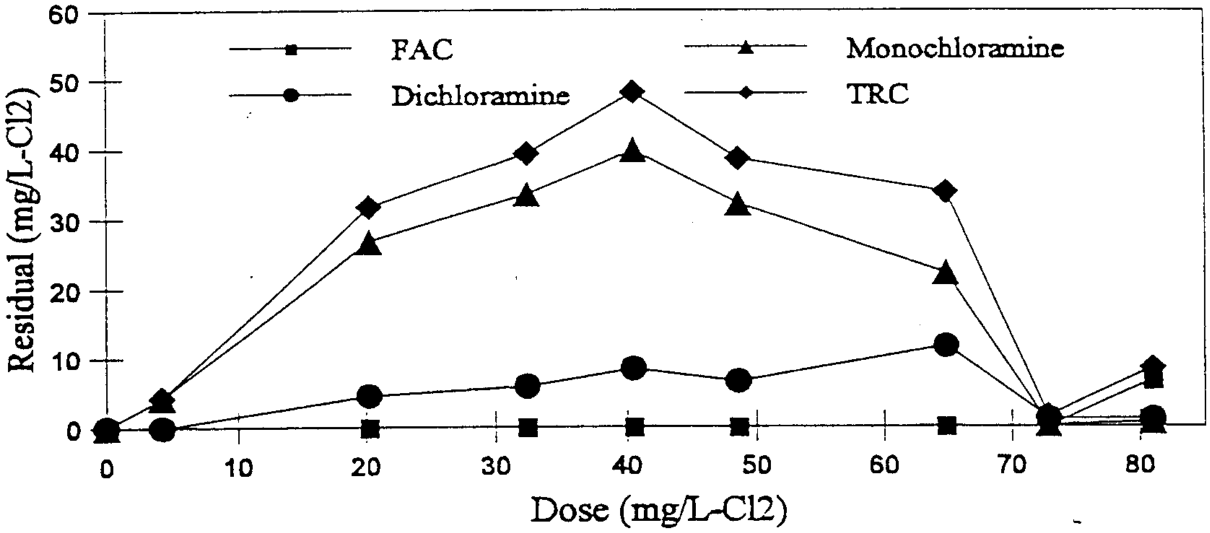
April 22, 1996 (8.80 mg/L NH_3-N, pH 7.39, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.00	0.25	0.00	0.00	0.25
4.00	3.84	0.00	3.04	0.80
32.00	27.90	0.00	25.70	2.10
40.00	37.82	0.10	33.02	4.80
44.00	37.90	0.00	33.40	4.50
48.00	38.65	0.15	34.10	4.40
60.00	36.10	0.10	24.40	11.60
68.00	17.14	0.20	6.30	10.84
80.00	7.80	5.20	0.20	2.40



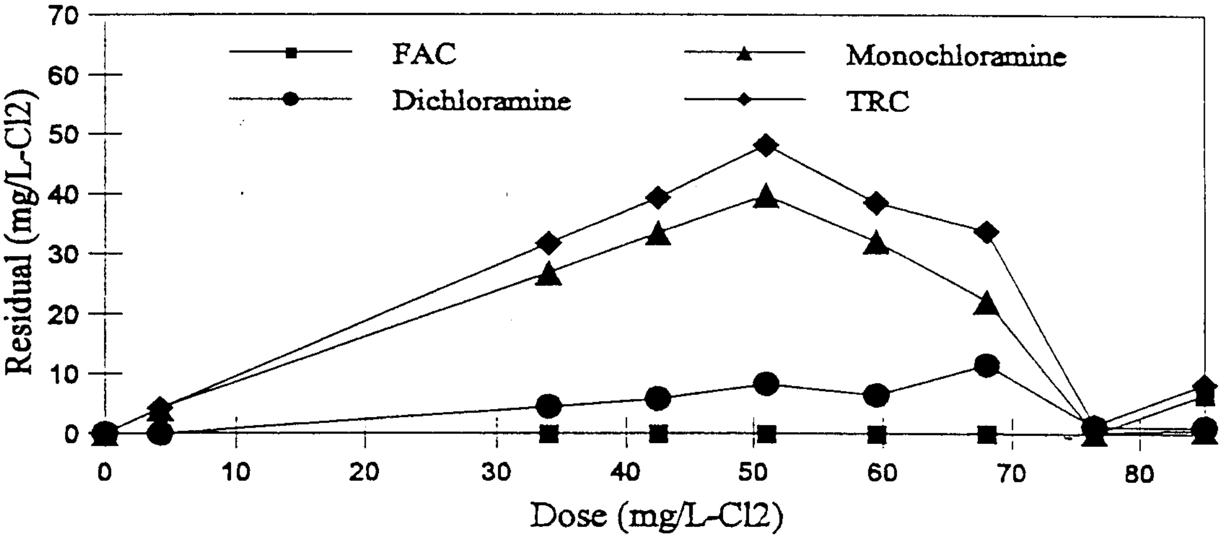
April 29, 1996 (8.18 mg/L NH_3-N, pH 7.47, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.00	0.00	0.00	0.00	0.00
4.25	4.20	0.10	4.20	0.00
20.25	31.7	0.00	26.80	4.48
32.40	39.32	0.00	33.52	5.80
40.50	48.10	0.00	39.80	8.30
48.60	38.54	0.00	32.10	6.44
64.80	33.8	0.10	22.20	11.60
72.90	1.50	0.00	0.30	1.20
81.00	8.32	6.58	0.64	1.10



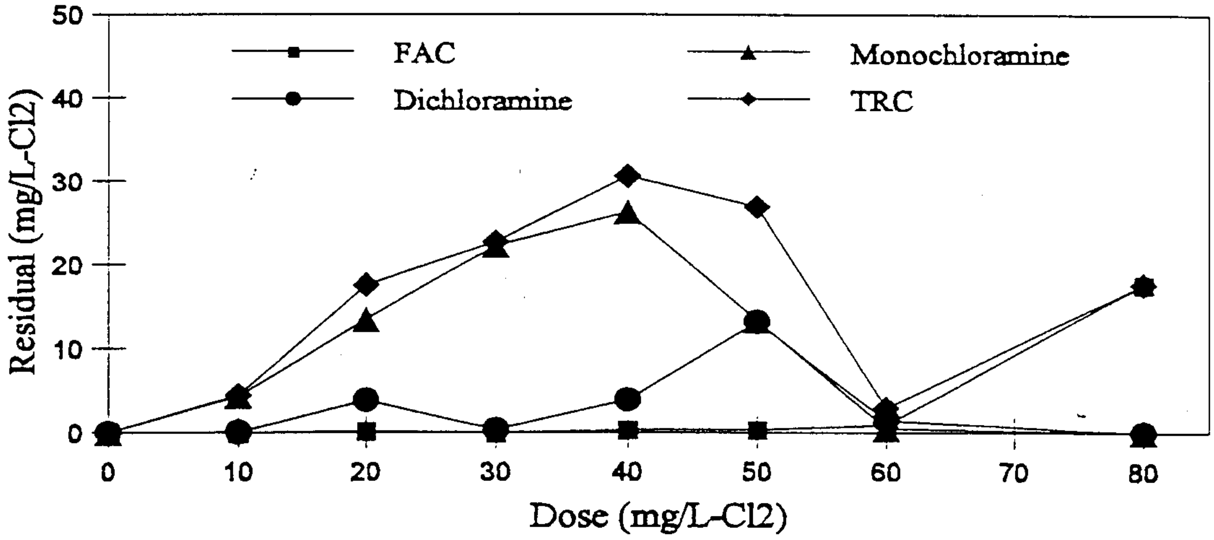
May 8, 1996 (10.63 mg/L NH_3-N, pH 7.41, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.00	0.00	0.00	0.00	0.00
4.25	4.20	0.10	4.20	0.00
34.00	31.7	0.00	26.80	4.48
42.50	39.32	0.00	33.52	5.80
51.00	48.10	0.00	39.80	8.30
59.50	38.54	0.00	32.10	6.44
68.00	33.8	0.10	22.20	11.60
76.50	1.50	0.00	0.30	1.20
85.00	8.32	6.58	0.64	1.10



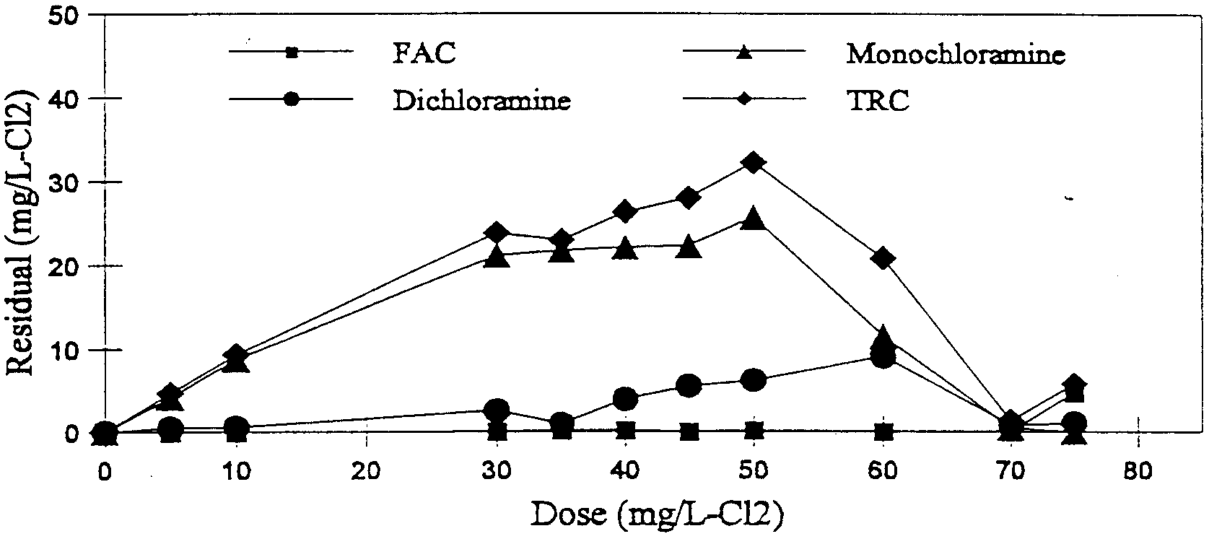
May 13, 1996 (9.79 mg/L NH_3-N, pH 7.47, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.00	0.00	0.00	0.00	0.00
10.00	4.46	0.00	4.36	0.10
20.00	17.56	0.20	13.46	3.90
30.00	22.70	0.00	22.30	0.40
40.00	30.62	0.36	26.30	3.96
50.00	26.94	0.40	13.34	13.20
60.00	2.90	0.90	0.50	1.50
80.00	17.64	17.64	0.00	0.00



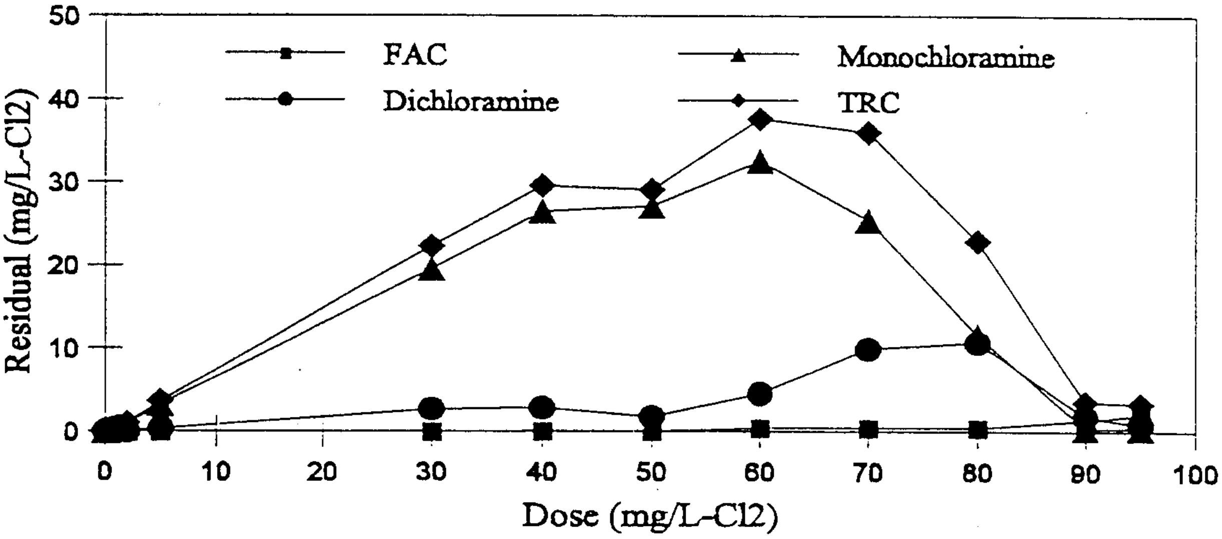
May 23, 1996 (6.60 mg/L NH_3-N, pH 7.69, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.00	0.00	0.00	0.00	0.00
5.00	4.70	0.00	4.20	0.50
10.00	9.40	0.00	8.80	0.60
30.00	23.90	0.10	21.20	2.60
35.00	23.00	0.20	21.80	1.00
40.00	26.40	0.20	22.20	4.00
45.00	28.10	0.10	22.40	5.60
50.00	32.30	0.20	25.80	6.30
60.00	20.90	0.10	11.60	9.20
70.00	1.40	0.10	0.50	0.80
75.00	5.90	4.80	0.00	1.10



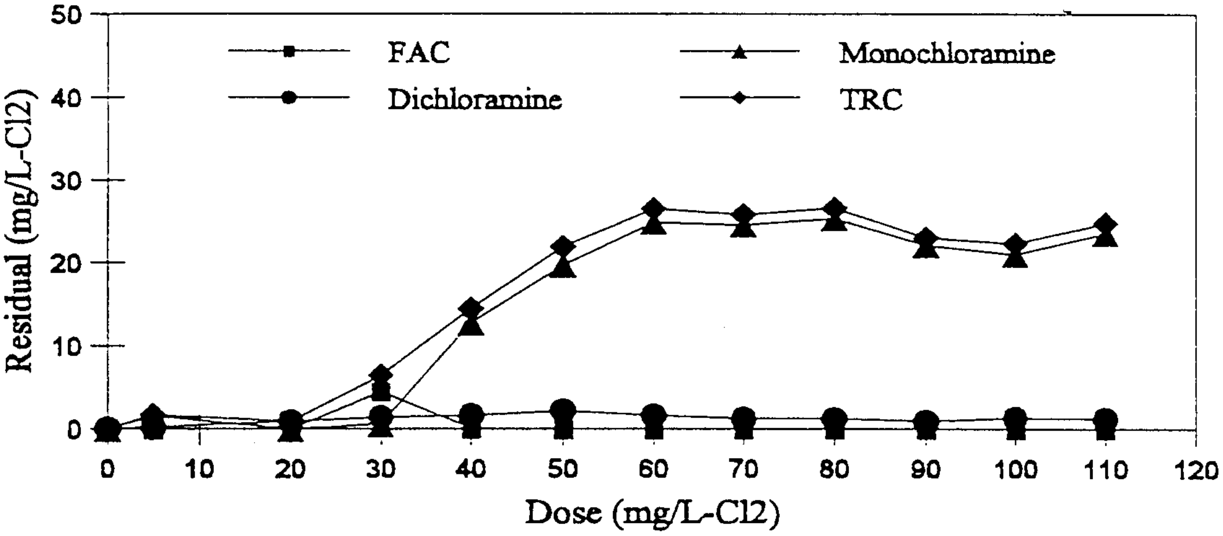
May 29, 1996 (9.75 mg/L NH_3-N, pH 7.66, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0.000	0.00	0.00	0.00	0.00
0.250	0.20	0.00	0.00	0.20
0.625	0.35	0.00	0.25	0.10
1.000	0.45	0.00	0.37	0.08
1.250	0.59	0.00	0.46	0.13
2.000	1.00	0.00	0.90	0.10
5.00	3.70	0.00	3.30	0.40
30.00	22.30	0.00	19.60	2.70
40.00	29.60	0.10	26.60	2.90
50.00	29.10	0.10	27.20	1.80
60.00	37.70	0.50	32.60	4.60
70.00	36.00	0.50	25.50	10.00
80.00	23.00	0.50	11.70	10.80
90.00	3.60	1.40	0.40	1.80
95.00	3.40	2.10	0.40	0.90



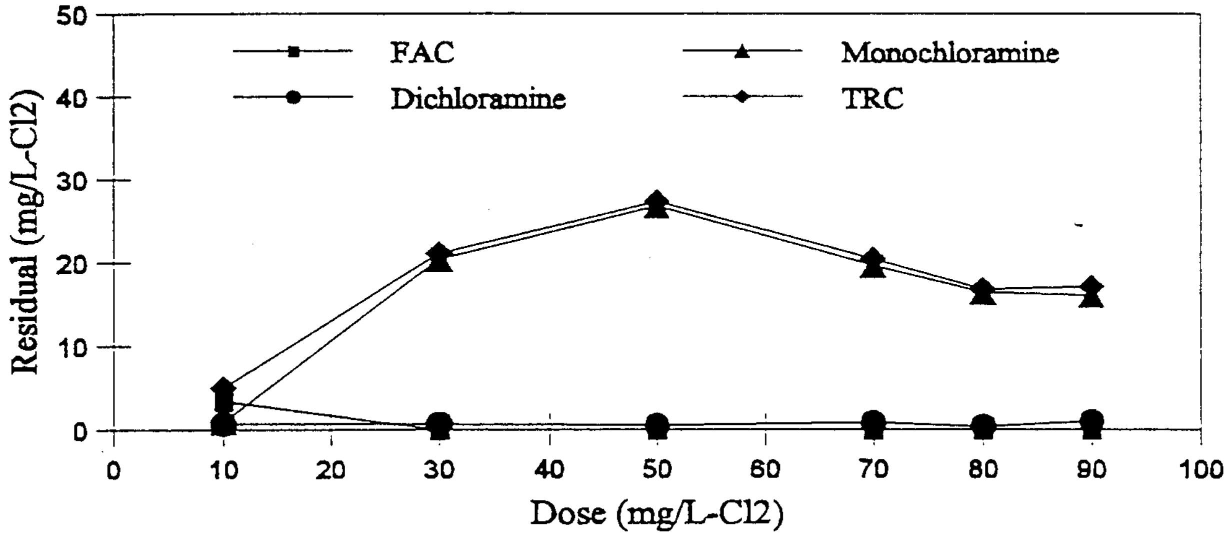
June 4, 1996 (6.56 mg/L NH_3-N, pH 7.65, 30 min contact)

	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
0	0.00	0.00	0.00	0.00
5	1.70	0.00	1.50	0.20
20	0.90	0.00	0.00	0.90
30	6.46	4.50	0.56	1.40
40	14.40	0.10	12.70	1.60
50	21.90	0.00	19.70	2.20
60	26.50	0.00	24.90	1.60
70	25.80	0.00	24.60	1.20
80	26.60	0.00	25.40	1.20
90	23.00	0.00	22.10	0.90
100	22.30	0.00	21.00	1.30
110	24.80	0.00	23.60	1.20



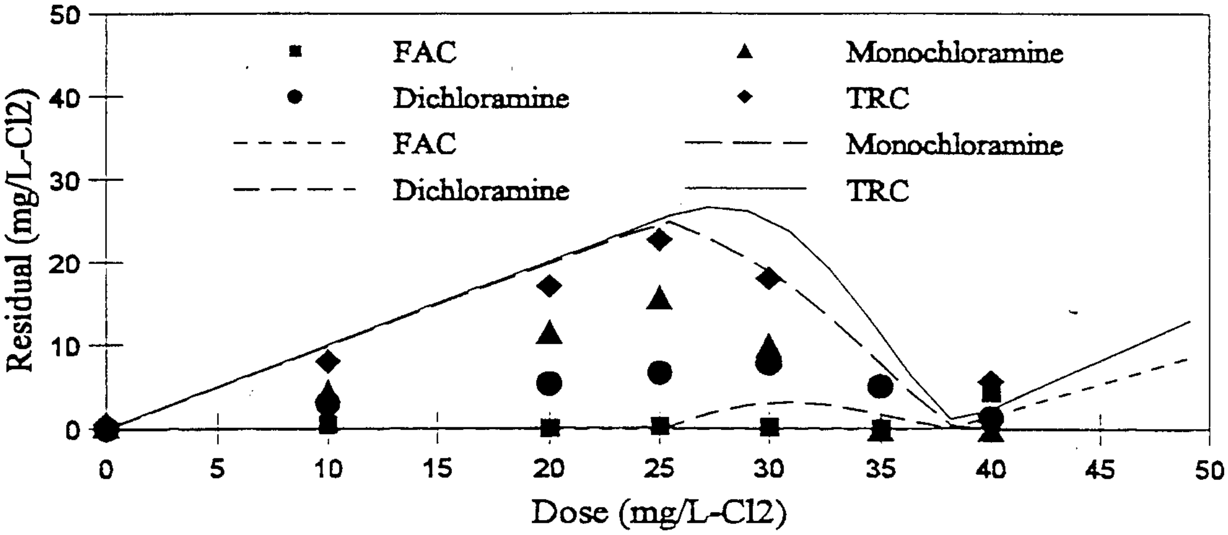
June 18, 1996 (0.07 mg/L NH_3-N, pH 7.61, 15 min contact)

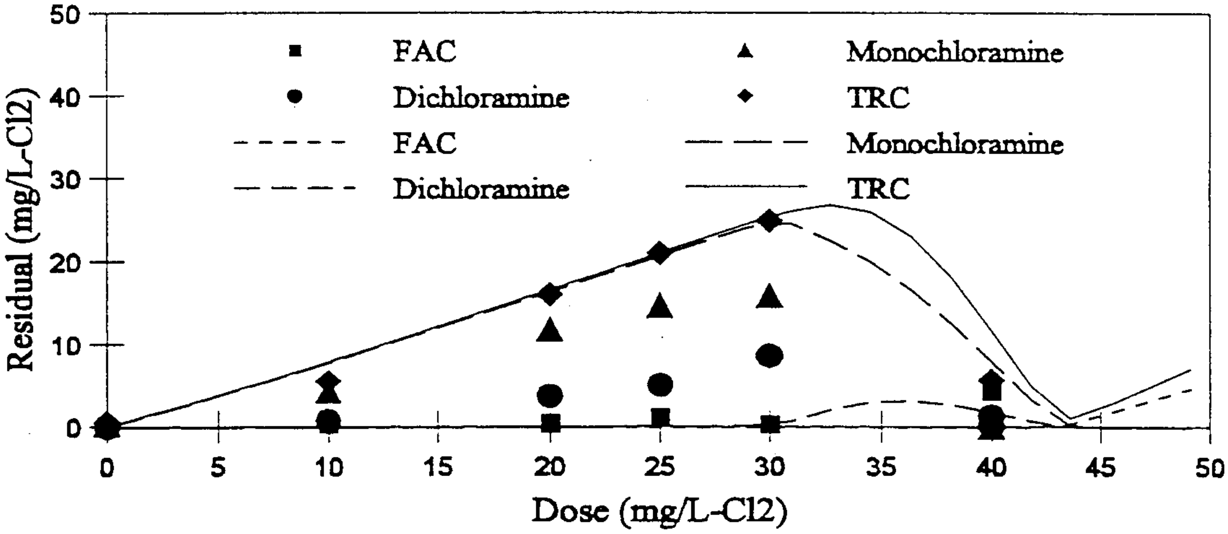
	Residual (mg/L)			
Dosage (mg/L)	TRC	FAC	Monochloramine	Dichloramine
10	5.00	3.40	0.90	0.70
30	21.10	0.00	20.40	0.70
50	27.30	0.00	26.80	0.50
70	20.40	0.00	19.60	0.80
80	16.80	0.00	16.40	0.40
90	17.10	0.00	16.10	1.00

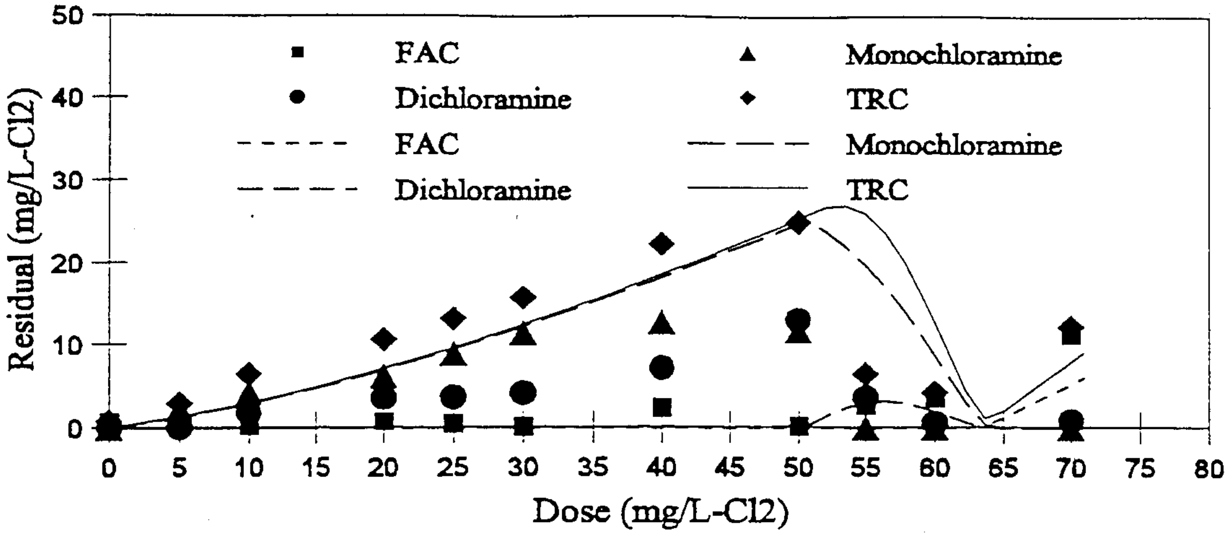


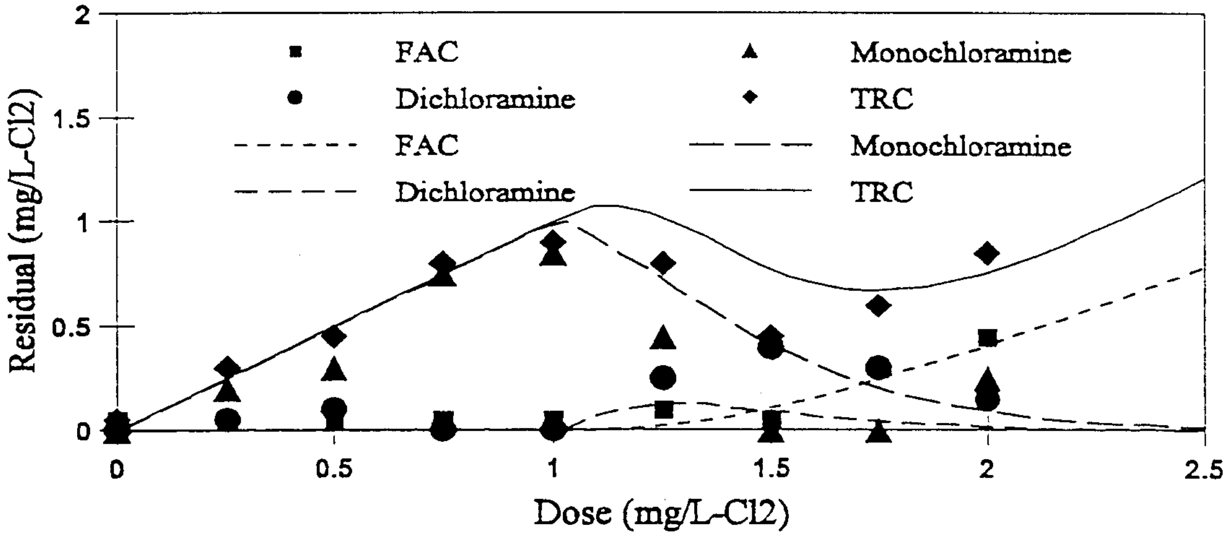
APPENDIX B: COMPARISON OF EXPERIMENTAL AND SIMULATED DATA

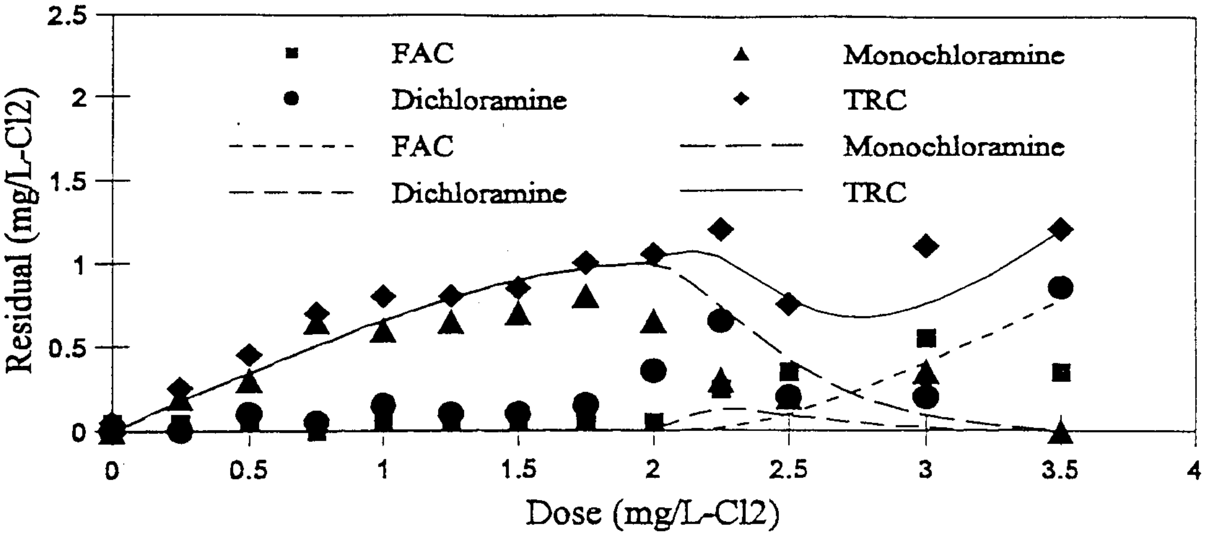
1. Contact time = 15 min

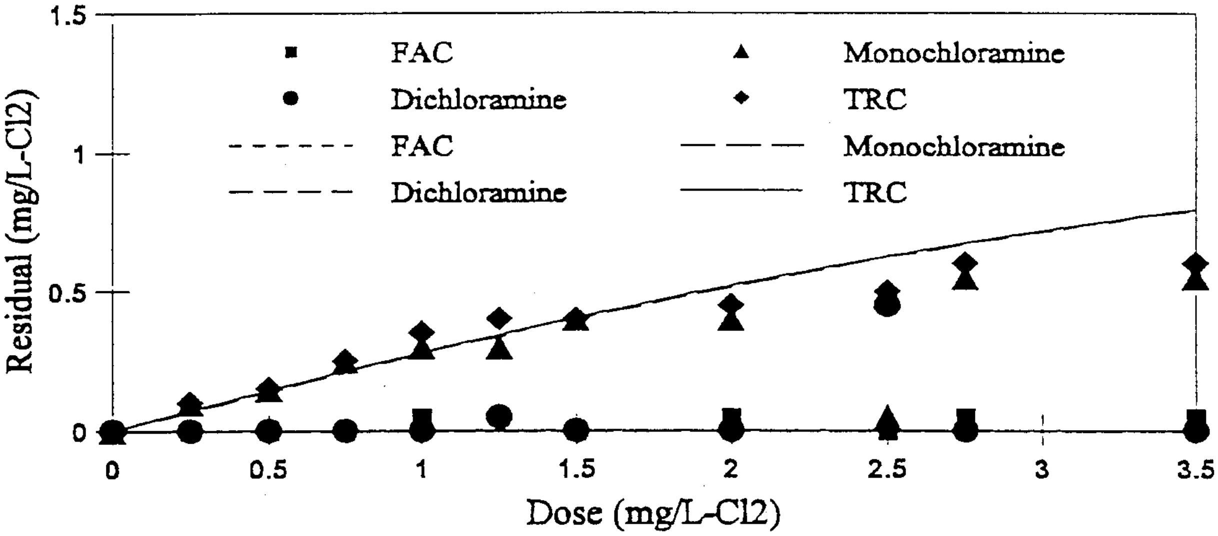

5 mg/L NH_3-N, 0 mg/L NO_2^--N

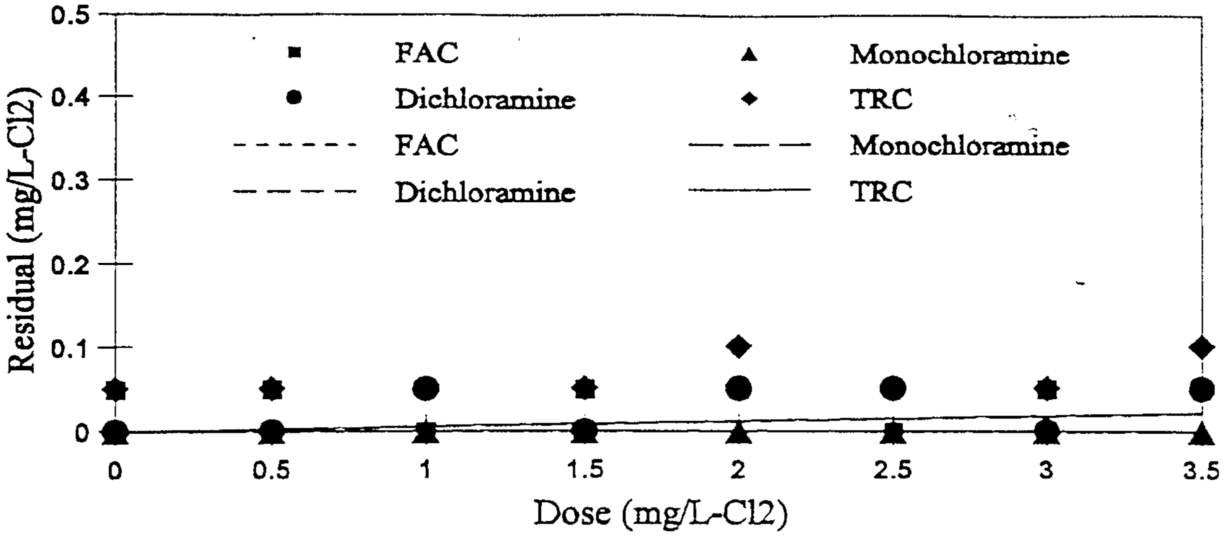

5 mg/L NH_3-N, 1 mg/L NO_2^--N


5 mg/L NH_3-N, 5 mg/L NO_2^--N

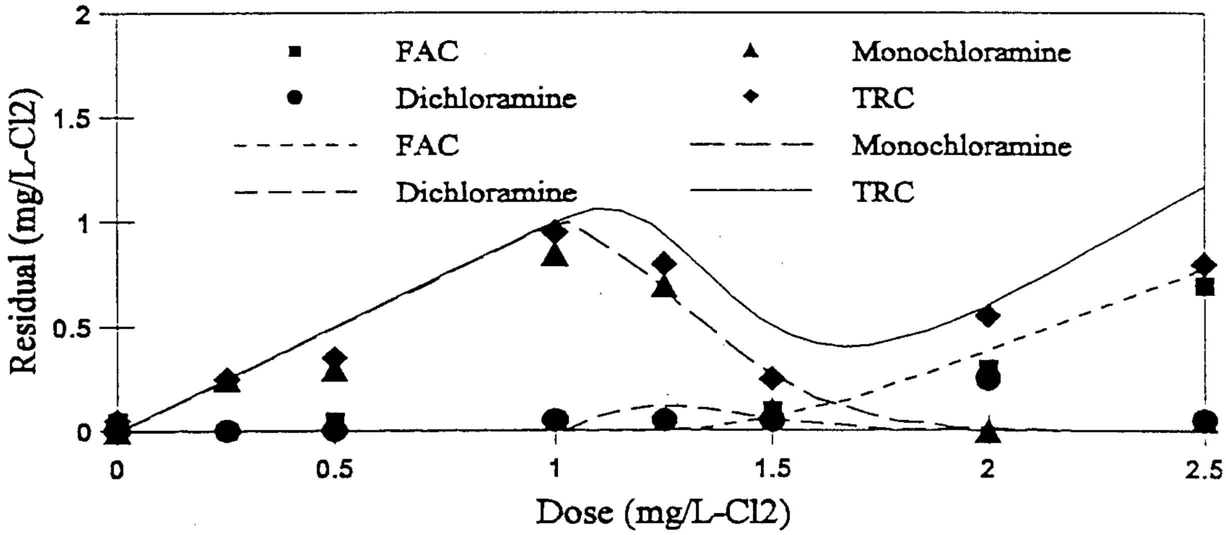

0.2 mg/L NH_3-N, 0 mg/L NO_2^--N

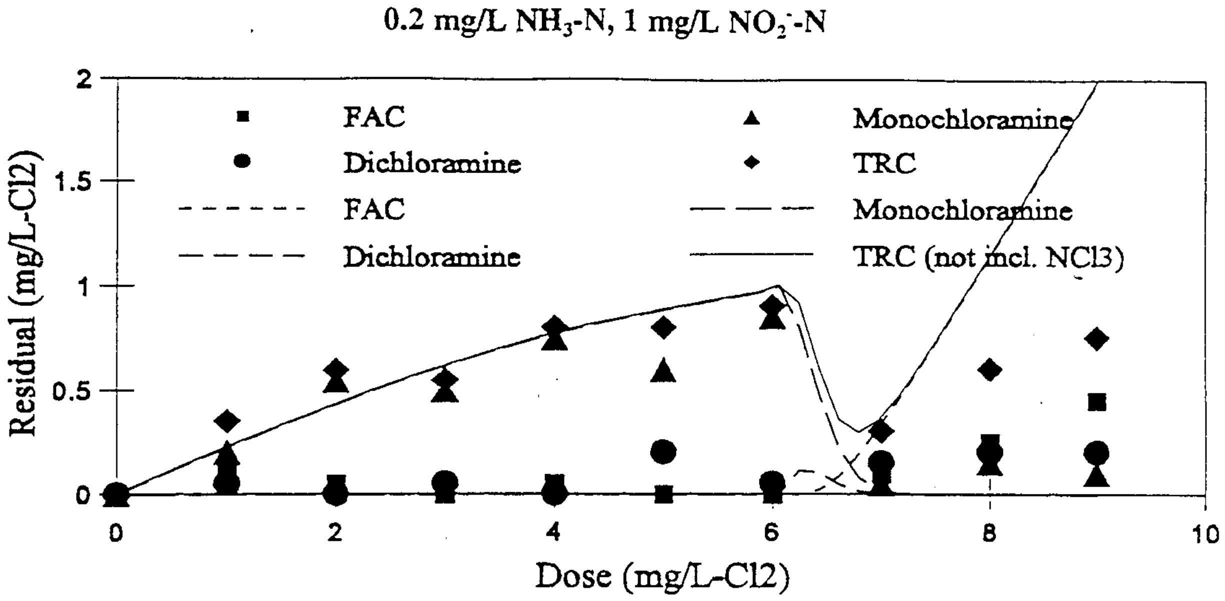

0.2 mg/L NH_3-N, 0.2 mg/L NO_2^--N


0.2 mg/L NH_3-N, 1 mg/L NO_2^--N

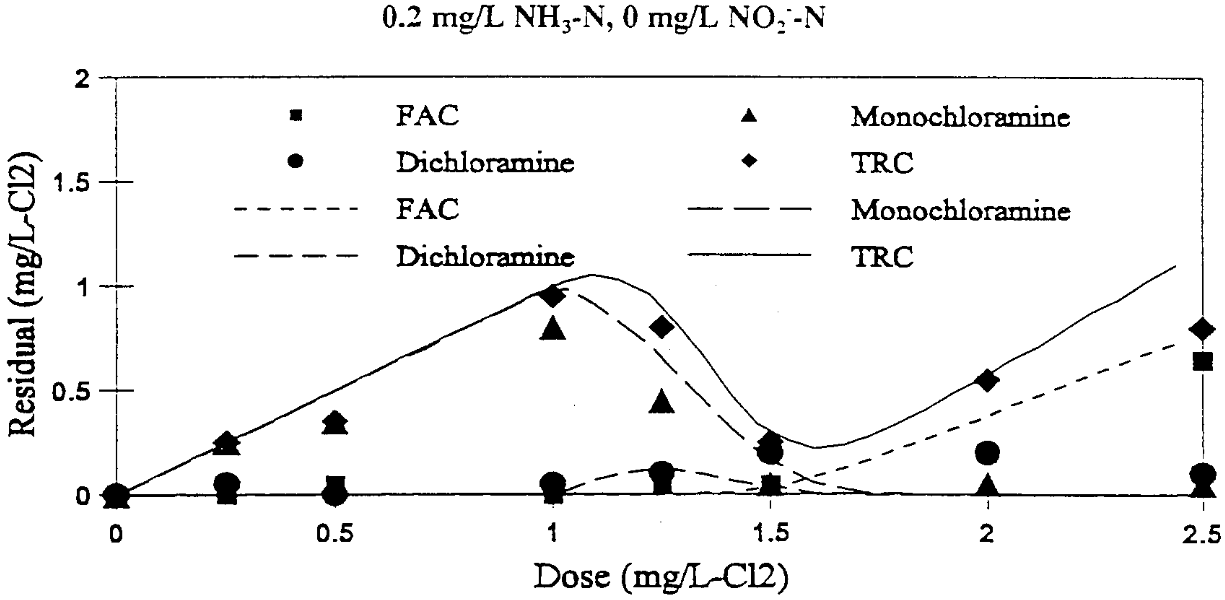

0.2 mg/L NH_3-N, 10 mg/L NO_2^--N

2. Contact time = 30 min

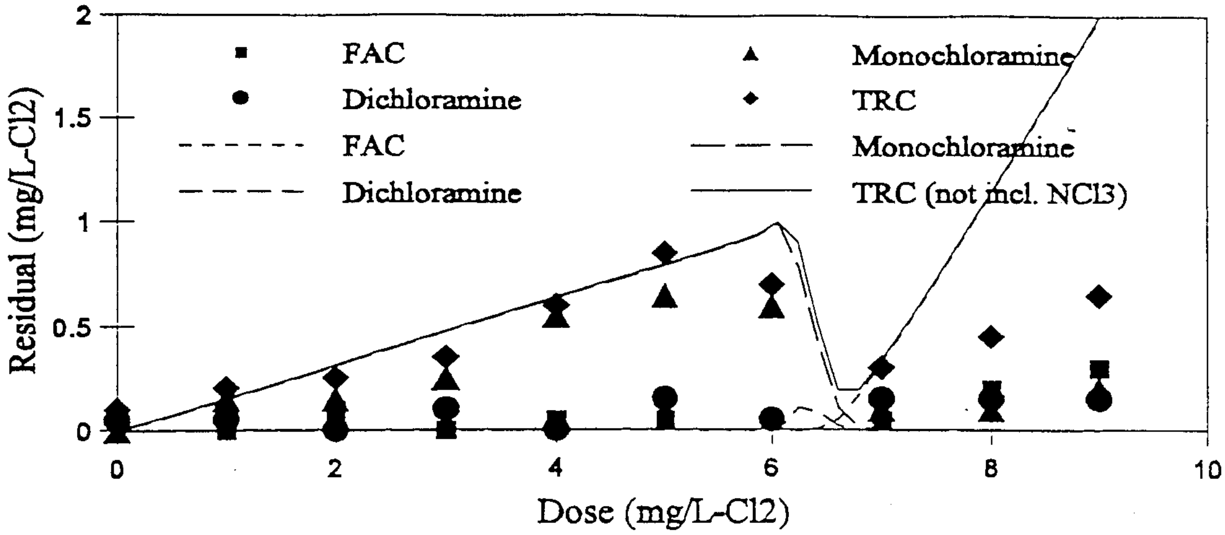

0.2 mg/L NH_3-N, 0 mg/L NO_2^--N



3. Contact time = 60 min

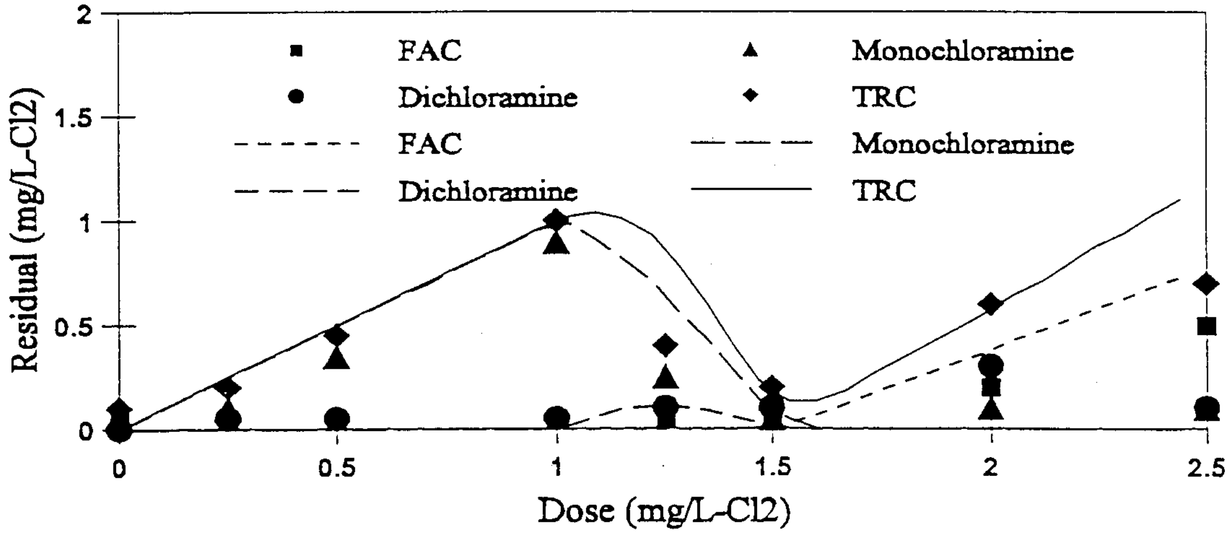


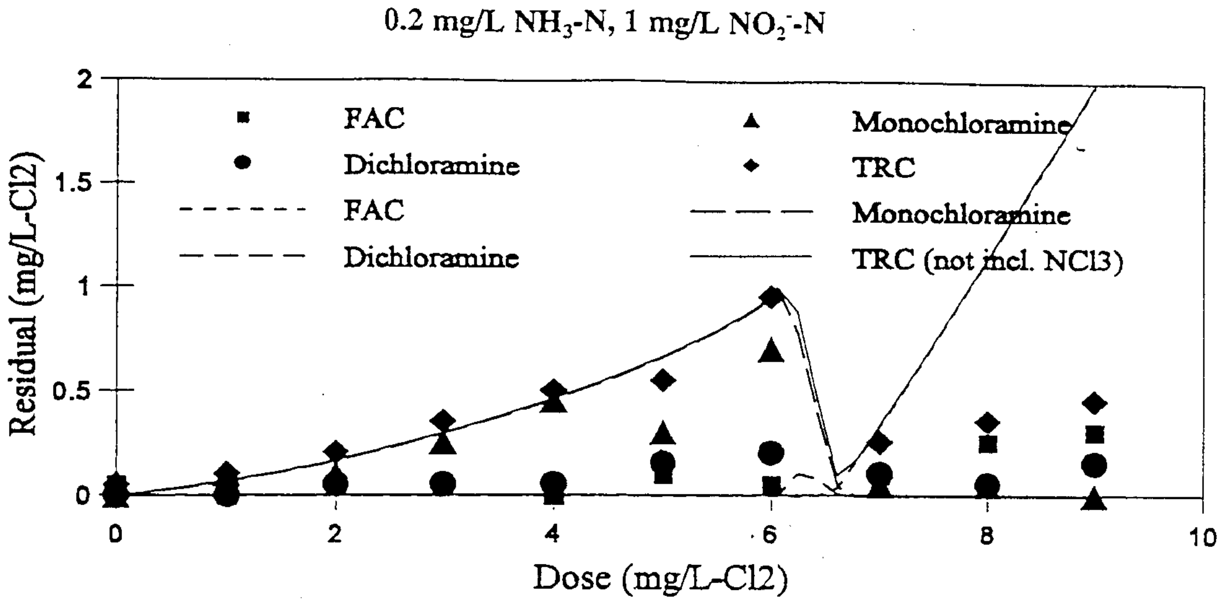
0.2 mg/L NH_3-N, 1 mg/L NO_2^--N



4. Contact time = 120 min

0.2 mg/L NH_3-N, 0 mg/L NO_2^--N




0.2 mg/L NH_3-N, 1 mg/L NO_2^--N
Residual (mg/L-Cl2)
Dose (mg/L-Cl2)
0
0.5
1
1.5
2
0
2
4
6
8
10
FAC
Monochloramine
Dichloramine
TRC
FAC
Monochloramine
Dichloramine
TRC (not incl. NCl3)

APPENDIX C: SIMPLIFIED KINETIC MODEL

The only three reactions involved in this model are:

1. $HOCl + NH_3 \rightarrow NH_2Cl + H_2O$ $\quad k_1 = 2.5\text{x}10^5\ mM^{-1}min^{-1}$
2. $HOCl + NO_2^- \rightarrow NO_3^- + Cl^- + H^+$ $\quad k_2 = 8.32\text{x}10^4\ mM^{-1}min^{-1}$
3. $NH_2Cl + NO_2^- \rightarrow NO_3^- + Cl^- + NH_4^+$ $\quad k_3 = 2.15\text{x}10^{-1}\ mM^{-1}min^{-1}$

$$f = \frac{k_1[NH_3]_0}{k_1[NH_3]_0 + k_2[NO_2^-]_0}$$

Reaction 1 occurs quickly. Assuming the fraction of added chlorine initially converted to monochloramine is *f*:

$$f = \text{initial rate of reaction 1/(initial rate of reaction 1 + initial rate of reaction 2)} \tag{1}$$

The mass balances for free chlorine, monochloramine, and nitrite in this system are:

nitrite consumed = HOCl consumed by nitrite + NH_2Cl consumed by nitrite

$$[NO_2^-]_0 - [NO_2^-] = (1 - f)[Cl]_T + (f[Cl]_T - [NH_2Cl]) \tag{2}$$

where: $[NO_2^-]_0$ = initial nitrite concentration

$[Cl]_T$ = total chlorine added (chlorine dose)

Rearrange equation 2:

$$[NO_2^-] = [NO_2^-]_0 - [Cl]_T + [NH_2Cl] \tag{3}$$

Since only trace free chlorine and dichloramine can be found for the rising leg of the breakpoint curve, and trichloramine forms only when the chlorine dose is close to the breakpoint, monochloramine is assumed equal to the TRC in this model.

After monochloramine is formed initially:

$$d[NH_2Cl]/dt = -k_3[NH_2Cl][NO_2^-] \tag{4}$$

The monochloramine concentration can be solved from equation 3 and 4 (with $[NH_2Cl]_0 = f[Cl]_T$):

$$[NH_2Cl] = \frac{[NO_2^-]_0 - [Cl]_T}{\left(\frac{[NO_2^-]_0 - [Cl]_T + f[Cl]_T}{f[Cl]_T}\right)e^{k_3([NO_2^-]_0 - [Cl]_T)t} - 1} \tag{5}$$

Nitrite concentrations were estimated by minimizing the sum of the squares between the monochloramine concentration predicted by equation 5 and the TRC data from the rising leg of the breakpoint curves.