

## ABSTRACT

The objective of this study was to determine and evaluate some of the factors that affect the formation and decay of disinfection by-products (DBPs), specifically trihalomethanes (THMs) and haloacetic acids (HAAs), in full-scale drinking water distribution systems. Five utilities throughout the United States were sampled 6–8 times over a period of 15 months. This paper addresses four of the five utilities chosen to participate in the study. Utilities were chosen based on source water characteristics, seasonal temperature changes, geographic location, type of secondary disinfectant utilized and several characteristics specific to each distribution system. Minimum levels of DBPs, THMs > 40 µg/L and HAAs > 20 µg/L, were also required for participation. In addition, each utility had a hydraulic model of their distribution system that was used to determine residence times at sampling locations in their distribution system. Although treatment processes were not considered in the selection of utilities, all the utilities chosen to participate in the study employed conventional treatment processes: coagulation, flocculation, sedimentation and filtration. Two utilities utilized free chlorine as their secondary disinfectant and two utilities utilized chloramines as their secondary disinfectant.

Sampling locations were chosen on the basis of residence time, pipe material, pipe diameter and other factors specific to each distribution system. Fourteen to sixteen sampling locations were chosen to represent the various conditions that were present in each distribution system. Samples collected were analyzed for pH, temperature, secondary disinfectant residual, assimilable organic carbon (AOC), total organic carbon (TOC), ultraviolet (UV) absorbance, heterotrophic plate counts (HPCs), THMs, HAAs, bromide and ammonia, nitrite and nitrate, where appropriate.

For those systems that utilized free chlorine, results show that chlorine residual decreased as residence time increased. In addition, THM and HAA concentrations increased as residence time increased. Evidence of biodegradation of HAAs at high residence times was observed at one utility. At sampling locations with high residence times, loss of chlorine residual and decreases in HAA concentration were coupled with increases in HPCs.

Data obtained for those utilities that utilized chloramines demonstrate that disinfectant residual remained constant throughout the distribution system, except at sampling locations where evidence of nitrification and HAA biodegradation were observed. Because of the periodic

addition of a second raw water source, the hydraulic model for one of the systems was rerun and new hydraulic scenarios were determined. Consequently, the residence times at each sampling location for this system were altered depending on flow and demand in the distribution system. Thus, for some scenarios, the total chlorine residual remained constant, while for others, a significant decrease in total chlorine residual was observed.

THM4 and HAA9 concentrations remained constant at both utilities when the disinfectant residual remained constant. However, at both utilities, a decrease in HAA9 concentrations was seen, particularly at those sampling locations that showed a decrease in total chlorine residual and elevated HPCs. These results are consistent with typical conditions that promote the biodegradation of HAAs. In one of the systems a decrease in THM4 concentration was seen at the same locations where HAA9 biodegradation occurred. Evidence of nitrification was seen at both utilities, specifically at locations with low total chlorine residual.

## ACKNOWLEDGEMENTS

I would first like to thank Dr. Singer for his guidance, in the classroom, as my research advisor and professionally. I will always be appreciative of his ability to understand that I am an engineer who doesn't want to be an engineer. I would also like to thank Dr. DiGiano and Dr. Characklis for giving their time to be on my master's defense committee.

I would like to thank the laboratory technicians and my fellow graduate students at the UNC Water and Wastewater Research Center. In particular, a big shout out and thank you to my PIC, Cora Nichols. Cora and I spent more hours together in close proximity, while enduring more miserable conditions than are humanly comfortable, and yet still managing to have a healthy respect for one another. Erika Depaz taught me the DBP analytical procedures that enabled me to do this work. Dan Gatti (especially Dan!) kept the GCs running the best he knew how and guided me through countless hours of struggle and confusion to a place of clarity. Thank you to the DubDub crew, both past and present, for the insight, the company and just plain fun. To the girls in Rosenau, here's to Caribou, Foster's and apple martinis.

I would like to thank the AWWARF 2770 project team for providing me the opportunity to do this work. I would especially like to thank Helene Baribeau and Lina Boulos of Carollo Engineers for their management of this project and for answering my millions of questions. In addition, a big thank you to all the utilities and their personnel for their sample collection and laboratory analyses. Finally, I would like to thank AWWARF for their financial support and the members of the AWWARF project advisory committee for their insight.

And last, but by no means least, I would like to thank all the family (especially my mom, dad, sisters and grandparents, who have no idea what I do, but ask anyway) and friends that lent me guidance and unending support through my time at UNC. They have been there to challenge and encourage me and remind me of what I can achieve and that failure is not a bad thing. I would not be here without them. Finally I would like to thank Troy Biggs, who has listened to me for two years and always unconditionally and unwaveringly supported me throughout this process. His humor, love and honesty help me get by.

## TABLE OF CONTENTS

INTRODUCTION .....	1
LITERATURE REVIEW .....	5
2.1 DISINFECTANT CHEMISTRY .....	5
2.1.1 Chlorine .....	5
2.1.2 Chloramines .....	6
2.2 DISINFECTION BY-PRODUCTS .....	7
2.2.1 Regulations .....	8
2.2.2 Water Quality and Treatment Factors Contributing to THM and HAA Formation .....	11
2.2.3 Distribution System Characteristics .....	13
2.3 BACTERIOLOGICAL GROWTH IN THE DISTRIBUTION SYSTEM .....	15
2.4 BIODEGRADATION OF HALOACETIC ACIDS .....	17
2.5 NITRIFICATION IN DISTRIBUTION SYSTEMS .....	18
MATERIALS AND METHODS .....	22
3.1 SELECTION OF UTILITIES .....	22
3.2 SELECTION OF SAMPLING LOCATIONS .....	22
3.3 GLASSWARE AND BOTTLE PREPARATION .....	23
3.4 SAMPLING PROTOCOL .....	24
3.5 ANALYTICAL PROCEDURES .....	26
3.5.1 Total Organic Carbon (TOC) .....	26
3.5.2 Ultraviolet (UV) Absorbance .....	27
3.5.3 Trihalomethanes (THM4) .....	27
3.5.4 Haloacetic Acids (HAA9) .....	30
RESULTS AND DISCUSSION .....	34
4.1 UTILITY C .....	34
4.1.1 Distribution System Sampling Locations .....	34
4.1.2 Distribution System Sampling Results .....	35
4.1.3 Total Chlorine Residual .....	38
4.1.4 Heterotrophic Plate Counts .....	39

4.1.5 Disinfection By-Product Formation.....	40
4.1.6 Nitrification.....	44
4.2 UTILITY A.....	46
4.2.1 Distribution System Sampling Locations .....	46
4.2.2 Distribution System Sampling Results .....	47
4.2.3 Chlorine Residual.....	50
4.2.4 Heterotrophic Plate Count.....	51
4.2.5 Disinfection By-Product Formation.....	52
4.3 UTILITY B.....	57
4.3.1 Distribution System Modeling.....	57
4.3.2 Distribution System Sampling Results .....	58
4.3.3 Chlorine Residual.....	61
4.3.4 Heterotrophic Plate Count.....	62
4.3.5 Disinfection By-Product Formation.....	63
4.4 UTILITY D.....	66
4.4.1 Distribution System Modeling.....	66
4.4.2 Distribution System Sampling Results .....	68
4.4.3 Chlorine Residual and Heterotrophic Plate Count.....	73
4.4.4 Disinfection By-Product Formation.....	77
4.4.5 Nitrification.....	84
4.5 SUMMARY.....	87
CONCLUSIONS AND RECOMMENDATIONS .....	89
5.1 CONCLUSIONS.....	89
5.2 RECOMMENDATIONS.....	91
REFERENCES .....	92
APPENDIX A.....	101
APPENDIX B.....	137
APPENDIX C .....	162
APPENDIX D.....	191

Table 4.22 Haloacetic acid (HAA) data (in $\mu\text{g/L}$ ) for Utility D for 4/08/03 .....	70
Table 4.23 pH, temperature and chlorine data for Utility D for 1/07/03 .....	71
Table 4.24 Organic carbon, microbiological, nitrogen and bromide data for Utility D for 1/07/03 .....	71
Table 4.25 Trihalomethane (THM) data (in $\mu\text{g/L}$ ) for Utility D for 1/07/03 .....	72
Table 4.26 Haloacetic acid (HAA) data (in $\mu\text{g/L}$ ) for Utility D for 1/07/03 .....	72

## LIST OF FIGURES

Figure 4.1 Total chlorine residual versus average residence time for Utility C for 10/21/03 .....	39
Figure 4.2 Total chlorine residual and HPCs versus average residence time for Utility C for 10/21/03 .....	40
Figure 4.3 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 10/21/03.....	41
Figure 4.4 THM4 and HAA9 versus total chlorine residual for Utility C for 10/21/03 .....	43
Figure 4.5 Nitrogen species versus average residence time for Utility C for 10/21/03.....	45
Figure 4.6 Total chlorine residual versus average residence time for Utility A for 9/23/03 .....	51
Figure 4.7 Total chlorine residual and HPC versus average residence time for Utility A for 9/23/03.....	52
Figure 4.8 THM4, HAA9 concentrations and total chlorine residual versus average residence time for Utility A for 9/23/03.....	53
Figure 4.9 THM4 and HAA9 concentration versus total chlorine residual for Utility A for 9/23/03.....	55
Figure 4.10 Changes in THM4 and HAA9 concentration versus changes in total chlorine residual in the distribution system for Utility A for all sampling dates. ....	55
Figure 4.11 Total chlorine residual versus average residence time for Utility B for 4/29/03. ....	62
Figure 4.12 Total chlorine residual and HPC versus average residence time for Utility B for 4/29/03 .....	63
Figure 4.13 THM4 and HAA9 concentration versus average residence time for Utility B for 4/29/03 .....	65
Figure 4.14 THM4 and HAA9 concentration versus total chlorine residual for Utility B for 4/29/03 .....	65
Figure 4.15 Total chlorine residual versus average residence time for Utility D for 4/08/03 .....	74
Figure 4.16 Total chlorine residual and HPC versus average residence time for Utility D for 4/08/03 .....	74
Figure 4.17 Total chlorine residual versus residence time for Utility D for 1/07/03.....	75
Figure 4.18 Total chlorine residual and HPC versus average residence time for Utility D for 1/07/03.....	76

Figure 4.19 THM4 concentration versus average residence time for Utility D for 4/08/03.....	77
Figure 4.20 HAA9 concentration versus average residence time for Utility D for 4/08/03.....	78
Figure 4.21 THM4, HAA9 concentrations and total chlorine residual versus average residence time for Utility D for 4/08/03.....	79
Figure 4.22 THM4 and total chlorine residual versus average residence time for Utility D for 1/07/03.....	80
Figure 4.23 THM4 speciation versus residence time for Utility D for 1/07/03.....	80
Figure 4.24 HAA9 and total chlorine residual versus average residence time for Utility D for 1/07/03.....	81
Figure 4.25 HAA9 speciation versus residence time for Utility D for 1/07/03.....	82
Figure 4.26 THM4 and HAA9 concentration versus average residence time for Utility D for 1/07/03.....	83
Figure 4.27 THM4 and HAA9 concentration versus total chlorine residual for Utility D for 1/07/03.....	83
Figure 4.28 Nitrogen species versus average residence time for Utility D for 4/08/03.....	84
Figure 4.29 Nitrogen species versus average residence time for Utility D for 1/07/03.....	85
Figure 4.30 Nitrogen species versus total chlorine residual for Utility D for 1/07/03.....	86
Figure 4.31 Chlorine residual and HPC for all utilities for all sampling dates.....	88

## CHAPTER 1

### INTRODUCTION

Discovery of the disinfecting powers of chlorine greatly increased the ability of water purveyors to protect consumers of public water supplies from exposure to disease-causing organisms. Disinfection of water for protection against microscopic pathogens has a long history of use in our society. Free chlorine was first used as a disinfectant in the early 1900s (USEPA 2000). In addition to their disinfection capabilities, disinfectants react with natural organic matter (NOM) to form disinfection by-products (DBPs). DBPs are formed via chemical reactions of halogens (usually chlorine and/or bromine) with the NOM found in raw water sources. Two classes of halogenated DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), comprise the majority of DBPs formed during treatment of drinking water. DBPs were discovered in the 1970s and epidemiologically linked to adverse human health effects. Increased risks of developing bladder and rectal cancers have been associated with exposure to THMs (Cantor et al. 1998, Hildesheim et al. 1998). In addition, several epidemiological studies have linked exposure to THMs with an increased risk of spontaneous abortion, neural tube defects, still-births, central nervous system defects, low birth weight and birth defects (Savitz, Andrews and Pastore 1994; Bove et al. 1995; Waller et al. 1998; Dodds et al. 1999).

Since the link was established between adverse human health effects and DBPs, the United States Environmental Protection Agency (EPA) has regulated THMs and HAAs. In order to prevent microbial re-growth in the distribution system, the EPA requires water utilities to maintain a disinfectant residual in treated drinking water as it leaves the water treatment plant (USEPA 1998). In addition, the EPA requires a detectable residual for at least 95% of the samples collected from the distribution system. Although the disinfectant residual is meant to protect against microbial regrowth, it is also available for reactions with other constituents in the water matrix, and can continue to react with NOM to form more THMs and HAAs. Under the Stage I Disinfectants/Disinfection By-Products Rule currently in effect, the EPA has set maximum contaminant levels (MCLs) for the four trihalomethanes (THM<sub>4</sub>) and five of the nine haloacetic acids (HAA<sub>5</sub>) of 0.08 mg/L and 0.06 mg/L, respectively (USEPA 2003). Compliance with these MCLs is based on a system-wide running annual average (RAA) of samples taken quarterly at four sampling locations within the distribution system. The proposal of new DBP

regulations (USEPA 2003) has prompted some utilities to change secondary disinfectants from free chlorine to chloramines.

Many factors affect the formation and speciation of THMs and HAAs, including disinfectant type and residual, concentration and properties of natural organic matter, contact time, temperature, pH and bromide concentration of the raw water source. Raw water characteristics, such as NOM and bromide concentration, and treatment practices, including disinfectant type and pH, have the greatest effect on the formation and speciation of DBPs in drinking water prior to its entry into the distribution system. Disinfectant residual, residence time, pH and temperature have the greatest effect on subsequent DBP formation in the distribution system.

THM and HAA formation have been shown to increase with increasing concentrations of NOM (Singer 1999). In addition to NOM, raw water bromide concentrations have an important effect on DBP speciation. Bromide tends to react with NOM faster than free chlorine, resulting in the formation of more heavily brominated species of THMs and HAAs. Temperature influences the formation and speciation of DBPs by affecting NOM and disinfection reaction kinetics. Formation kinetics tend to increase as temperatures increase. THM formation (especially chloroform formation), as well as HAA formation, have been found to be higher at warmer temperatures (Krasner et al. 1996, Singer 2001). THM4 concentrations increase as pH increases and concentrations of certain HAA9 species increase as pH decreases for typical water treatment pH ranges (Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Symons et al. 1996; Singer 1999; Singer 2001; Singer 2002; Liang and Singer 2003).

Free chlorine has a greater tendency than chloramines to participate in substitution reactions. Consequently, use of free chlorine as a secondary disinfectant can result in higher DBP concentrations (Wolfe, Ward and Olson 1984; Johnson and Jensen 1986; Baribeau et al. 2000; Singer 2001; Vikesland, Pzekin and Valentine 2001). Typically, chloramines are more stable than free chlorine in the distribution system. The use of chloramines as a secondary disinfectant has been shown to impede the continued formation of THMs and HAAs in the distribution system. DBP formation may still occur to a limited degree when chloramines are used due to the presence of small amounts of free chlorine (Johnson and Jensen 1986).

Contact time, or residence time, plays an important role in DBP formation. Higher residence times allow more complete reactions of disinfectants with other reactants in the water

matrix. THM and HAA concentrations have been found to increase in the presence of a free chlorine residual as residence time increases (Bellar, Lichtenberg and Kroner 1974; Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Krasner et al. 1996; Baribeau et al. 2001; Singer 2001; Dickenson, Work and Summers 2002; Pope et al. 2002). Diurnal variations in water demand alters contact time and can also change observed DBP patterns. Singer (2001) found that variations of greater than 50% have been observed and attributed to diurnal variations in water demand. In addition, decreases in HAA concentrations, believed to be a result of biodegradation, have been documented at laboratory scale and in full-scale distribution systems (van der Ploeg, van Hall and Janssen 1991; Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995; Williams, Williams and Gordon 1996; LeBel, Benoit and Williams 1997; Chen and Wiesel 1998). HAA9 degradation has been shown to correspond with locations of low disinfectant residual and high heterotrophic plate counts (HPCs) (Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995). Warmer temperatures have also been correlated to HAA9 biodegradation (Williams, Williams and Gordon 1995; Chen and Wiesel 1998; Baribeau et al. 2000).

Reactions of the disinfectant residual with pipe walls and biofilms affect DBP formation and decay. The reactions of the disinfectant residual with the pipe wall produces corrosion by-products (Vasconcelos et al. 1997) which may provide reservoirs of organic matter that might promote DBP formation. The surface-area-to-volume ratio has been shown to affect disinfectant decay in smaller diameter pipes; disinfectant residual decay increases as surface-area-to-volume ratio increases (Vasconcelos et al. 1997, Prevost et al. 1998, Baribeau et al. 2000).

Despite the presence of disinfectant residuals, biological regrowth often occurs in distribution systems and may cause a multitude of problems, including an increase in disinfectant demand and corrosion rates and adverse human health risks. HPCs are often used as indicators of biological activity in a distribution system. Utilities that chloramine may periodically switch to free chlorine in order to limit the microbial regrowth. LeChevallier et al. (1996) found that temperature is the most important factor controlling microbial growth in drinking water. Temperature affects microbial growth rates and disinfectant decay and inactivation kinetics, among other factors. As free chlorine residual increases, HPCs decrease (Prevost et al. 1998, Zhang and DiGiano 2002). HPCs have also been found to increase with increasing residence time (Zhang and DiGiano 2002).

Although chloramination may limit further formation of DBPs in distribution systems, chloramination is not without issues. Biological nitrification can occur in chloraminated distribution systems. Typical indications of nitrification include a decrease in chloramine residual, an increase in HPCs, a decrease in ammonia concentrations and an increase in nitrite and nitrate concentrations (Lieu, Wolfe and Means 1993; Skadsen 1993; Odell et al. 1996; Wilczak et al. 1996; Harrington et al. 2002; Skadsen 2002; Pintar and Slawson 2003). Long residence times tend to promote nitrification by allowing nitrifying bacteria to grow and to acclimate to pH conditions and the presence of chloramines (Wilczak et al. 1996). Dead ends, oversized mains, reservoir design and operation (short circuiting or poor turnover), and extensive distribution networks increase residence time and enhance the conditions conducive to for nitrification (Odell et al. 1996).

The objective of this study was to examine some of the factors that affect the formation and decay of THMs and HAAs in full-scale distribution systems on a more comprehensive basis than in previous studies. Disinfectant type and residual, residence time, temperature, occurrence of HPCs and nitrification were investigated. Four utilities were selected based on a number of criteria, including type of secondary disinfectant utilized, variations in seasonal temperature, geographic locations, NOM concentrations, evidence of microbial activity and distribution system characteristics. This study was part of a larger project sponsored by the American Water Works Association Research Foundation (AWWARF; AWWARF #2770) and overseen by Carollo Engineers of East Fountain Valley, CA.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 DISINFECTANT CHEMISTRY

Free chlorine was first used as a disinfectant in the early 1900s (USEPA 2000). Other widely used disinfectants in water treatment include chlorine dioxide, chloramines, ozone and ultraviolet (UV) irradiation. In order to prevent microbial regrowth in the distribution system, the EPA requires water utilities to maintain a disinfectant residual in the water (USEPA 1998). Ozone and UV do not provide a stable or persistent residual, thus most plants use free chlorine or combined chlorine (monochloramine).

##### 2.1.1 Chlorine

Chlorine is used as both a primary and secondary disinfectant. When used as a primary disinfectant, it may also be used as an oxidant to control aesthetic qualities and remove dissolved iron, manganese and hydrogen sulfide. As a secondary disinfectant, it is used to inactivate pathogens in water mains and storage tanks and preserve pipeline capacity by reducing biofilm growth (Vasconcelos et al. 1997). When chlorine is added to water, it rapidly hydrolyzes via reaction 2.1 in which hypochlorous acid (HOCl) and chloride are formed (Wolfe, Ward and Olson 1984):



HOCl further dissociates to form the hypochlorite ion (OCl<sup>-</sup>):

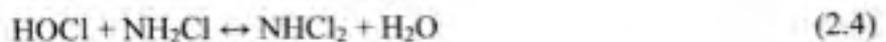


At pH 7.5, hypochlorous acid and hypochlorite exist at roughly equal concentrations (Wolfe, Ward and Olson 1984).

Free chlorine is a strong oxidant and can be readily consumed in the distribution system by reactions with organic and inorganic substances in the bulk phase, biofilms on the pipe wall, and the pipe wall itself (Vasconcelos et al. 1997; Kiene, Lu and Levi 1998; Baribeau et al. 2001).

### 2.1.2 Chloramines

Monochloramine, or combined chlorine, is typically used as a secondary disinfectant. Chloramines are formed by the addition of ammonia to treated water containing free chlorine. Chloramines are less reactive than free chlorine and therefore persist to a greater degree than free chlorine in water distribution systems (Wolfe, Ward and Olson 1984; Vikesland, Pzekin and Valentine 2001). They are also reported to have a better ability to penetrate biofilms (LeChevallier, Cawthon and Lee 1988) because they react more slowly than free chlorine (Wolfe, Ward and Olson 1984). When ammonia is added to treated water containing hypochlorous acid, monochloramine ( $\text{NH}_2\text{Cl}$ ), dichloramine ( $\text{NHCl}_2$ ) and trichloramine ( $\text{NCl}_3$ ) are formed via the following reactions (Wolfe, Ward and Olson 1984):



The amount of monochloramine formed is dependent on the pH of the water and the chlorine-to-ammonia ( $\text{Cl}_2:\text{N}$ ) ratio. The larger the  $\text{Cl}_2:\text{N}$  ratio, the faster the oxidation of ammonia occurs (Vikesland, Pzekin and Valentine 2001). As pH decreases and  $\text{Cl}_2:\text{N}$  increases, the ammonia molecule becomes more heavily chlorinated (Wolfe, Ward and Olson 1984). Under traditional water treatment conditions, monochloramine is the predominant and most desirable species formed. Monochloramine is produced within seconds in the pH range of 7–9 (Wolfe, Ward and Olson 1984). Formation of dichloramine and trichloramine should be avoided since a chlorinous taste occurs at concentrations above 0.8 and 0.02 mg/L, respectively (Wolfe, Ward and Olson 1984). The optimal  $\text{Cl}_2:\text{N}$  ratio for producing monochloramine is 5:1 on a weight basis, but a  $\text{Cl}_2:\text{N}$  ratio of  $\leq 5:1$  is often used to avoid loss of chlorine residual by breakpoint reactions (Wolfe, Ward and Olson 1984).

Monochloramine is inherently unstable, even at neutral pH values (Vikesland, Ozekin and Valentine 1998) and can slowly decompose via a series of reactions which result in the oxidation of ammonia and the reduction of active chlorine in a process known as

autodecomposition (Vikesland, Ozekin and Valentine 1998). Autodecomposition results in the production of nitrogen gas and small quantities of nitrate (Vikesland, Ozekin and Valentine 1998; Duirk, Whitney and Valentine 2002). In some instances chloramine loss has also been attributed to reactions with NOM and certain inorganic substance like bromide (Vikesland, Ozekin and Valentine 1998; Duirk, Whitney and Valentine 2002).

## 2.2 DISINFECTION BY-PRODUCTS

Although chlorine-containing disinfectants are important in maintaining the microbial integrity of distribution systems, free chlorine and chloramines have been shown to react with NOM to form halogenated DBPs. There are many different classes of halogen-containing DBPs, the sum of which are called total organic halides (TOX). Some of these DBPs have been shown to have potentially adverse human health effects. The EPA has established MCLs for two classes of DBPs, THMs and HAAs, that are produced from water chlorination. The formation of these two classes of DBPs depends on raw water characteristics, treatment practices, and distribution system characteristics. The following is a general equation that demonstrates the formation of these two classes of DBPs (Singer 1994):



Bromide is usually naturally-occurring and is present depending on total dissolved solid concentrations and salt water intrusion conditions. NOM is derived from decayed vegetation and is chiefly composed of dissolved organic carbon. Table 2.1 presents the individual species of THMs and HAAs.

Table 2.1

Trihalomethanes (THMs) and Haloacetic Acids (HAAs)	
DBP Class	Species
Trihalomethanes	Chloroform (CHCl <sub>3</sub> )
	Bromodichloromethane (CHBrCl <sub>2</sub> )
	Dibromochloromethane (CHBr <sub>2</sub> Cl)
	Bromoform (CHBr <sub>3</sub> )
Haloacetic Acids	Trichloroacetic acid (Cl <sub>3</sub> AA)
	Tribromoacetic acid (Br <sub>3</sub> AA)
	Bromodichloroacetic acid (BrCl <sub>2</sub> AA)
	Dibromochloroacetic acid (Br <sub>2</sub> ClAA)
	Dichloroacetic acid (Cl <sub>2</sub> AA)
	Dibromoacetic acid (Br <sub>2</sub> AA)
	Bromochloroacetic acid (BrClAA)
	Monochloroacetic acid (ClAA)
	Monobromoacetic acid (BrAA)

### 2.2.1 Regulations

Simultaneous discoveries of THMs were made independently in 1974 by Rook (1974) and Bellar and Lichtenberg (1974). In 1976, the National Cancer Institute established chloroform as a carcinogen (NCI 1976), which ultimately led to the promulgation of the Interim Trihalomethane Rule by the EPA in 1979 (USEPA 1979, Singer 1993). The Interim Trihalomethane Rule established an MCL of 0.01 mg/L for the sum of the THM4: chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl) and bromoform (CHBr<sub>3</sub>) (USEPA 1979). The rule applied to systems that served 10,000 people or more. Compliance was demonstrated by measuring THMs at four locations in the distribution system on a quarterly basis for each treatment plant and computing a running annual average of the THM4 concentrations.

Since the promulgation of the Interim Trihalomethane Rule, additional epidemiological studies have been undertaken to determine the health effects associated with exposure to THMs. Increased risks of developing bladder and rectal cancers have been associated with exposure to THMs (Cantor et al. 1998, Hildesheim et al. 1998). In addition, several epidemiological studies have linked exposure to THMs with an increased risk of spontaneous abortion, neural tube

defects, still-births, central nervous system defects, low birth weight and birth defects (Savitz, Andrews and Pastore 1994; Bove et al. 1995; Waller et al. 1998; Dodds et al. 1999). Most of the studies have only considered ingestion of tap water as the route of exposure. Recent studies have indicated that bathing, showering and hand-washing of dishes may also increase exposure due to the volatile nature of THMs (Backer et al. 2000, Singer et al. 2003).

As named, the Interim Trihalomethane Rule was established to immediately control exposure to THMs in the interim while lawmakers, scientists and stakeholders could determine appropriate long-term control measures and limits to place on THMs and other DBPs.

#### *2.2.1.1 Stage I Disinfectants/Disinfection By-Products Rule*

In 1996, the Safe Drinking Water Act was amended to include the Stage I Disinfectants/Disinfection By-Products (D/DBP) Rule and the Interim Enhanced Surface Water Treatment Rule (USEPA 1998). After a negotiating process, the EPA promulgated the final Stage I D/DBP Rule in December of 1998. The new requirements lowered the MCL for THM4 to 0.08 mg/L and included, for the first time, an MCL for HAA5, of 0.06 mg/L (USEPA 1998). Research performed in the intervening years after the Interim THM Rule indicated the HAAs were the next largest fraction of all the halogenated DBPs (Singer 1993). Although the HAA class contains nine haloacetic acids, the EPA chose to regulate only mono-, di- and trichloroacetic acids and mono- and dibromoacetic acids. Based on limited occurrence data and the inability to accurately measure the four remaining HAAs, the EPA did not feel compelled to include them in the Stage I D/DBP Rule (Singer 1993). The Stage I D/DBP Rule established MCLs for bromate and chlorite at 10 µg/L and 1 mg/L, respectively, and maximum residual disinfectant levels (MRDLs) for chlorine, chloramines and chlorine dioxide (USEPA 1998). The Stage I D/DBP Rule requires that systems serving less than 10,000 people must also comply with the new MCLs (USEPA 1998). Compliance is based on a running annual average of quarterly samples taken at four locations throughout the distribution system per treatment plant, three from average residence times and one from a remote location in the distribution system (USEPA 1998).

Economic and feasibility issues were considered during the negotiations for the new THM4 limits. It was believed that reduction from 0.1 mg/L to 0.08 mg/L would offer more

protection to consumers but would not have detrimental economic impacts on the larger water utilities (Singer 1993, USEPA 1998) .

#### *2.2.1.2 Stage II Disinfectants/Disinfection By-Products Rule*

The Interim Trihalomethane Rule and the Stage I D/DBP Rule regulated THMs and HAAs on running annual averages based on samples taken in the distribution system from one remote location and three locations representing average conditions. Recent studies have found that adverse health effects associated with DBP exposure are due not only to long-term exposure and that the health effects are not only cancer-related. Links to spontaneous abortion in pregnant women, along with other fetal health-related issues may be due to short-term or acute exposure to DBPs (Savitz, Andrews and Pastore 1994; Waller et al. 1998; Dodds et al. 1999). In addition, locations of maximum THM concentrations may not be locations of maximum HAA concentrations (Boulos et al. 2003).

The Stage II D/DBP Rule includes an Initial Distribution System Evaluation that was incorporated so that utilities can conduct an evaluation of their distribution system to identify locations with high or peak DBP concentrations (USEPA 2003). The utilities are required to locate maximum THM and HAA locations. Once these locations are established, distribution systems are to be sampled quarterly from four locations at which peak THM4 and HAA5 concentrations occur (USEPA 2003). Instead of a single system-wide running annual average, locational running annual averages (LRAAs) are calculated. MCLs for THMs and HAA5 remain at 0.06 mg/L and 0.08 mg/L, respectively, but they must be met at each location (USEPA 2003). By requiring utilities to find locations that may have DBP concentrations higher than the MCLs and to reduce conditions that may contribute to high DBP concentrations, the new rule is designed to protect consumers that may consume or utilize drinking water at these locations.

## 2.2.2 Water Quality and Treatment Factors Contributing to THM and HAA Formation

Raw water quality, such as NOM and bromide concentrations, pH and temperature, and treatment practices, including disinfectant type and dose, have the greatest effect on the formation and speciation of DBPs in drinking water prior to its entry into the distribution system. Disinfectant type and residual, residence time, pH and temperature have the greatest effect on subsequent DBP formation and decay in the distribution system.

NOM is a heterogeneous mix of microbially decayed plant detritus chiefly composed of dissolved organic carbon (Croue et al. 1999). NOM can be operationally categorized into three fractions: hydrophobic, hydrophilic and transphillic. Hydrophobic material has been further classified as humic or fulvic acids (Croue et al. 1999). Surrogate measurements for NOM can be made by measuring total organic carbon (TOC), dissolved organic carbon (DOC) and/or ultraviolet (UV) absorbance.

THM and HAA formation have been shown to increase with increasing concentrations of NOM (Singer, 1999). In addition, the hydrophobic fraction of NOM in raw water, particularly humic acids, plays an important role in DBP formation (Croue et al. 1999). Hydrophobic NOM tends to yield higher THM and HAA formation potentials than hydrophilic NOM (Croue et al. 1999, Liang and Singer 2003). High molecular weight humic fractions yield higher chloroform concentrations than fulvic fractions (Peters, Young and Perry 1980; Croue et al. 1999). In water from the same source, humic acids on a per carbon basis consume more chlorine and produce more TOX, chloroform, trichloroacetic acids and dichloroacetic acids than fulvic acids (Reckhow, Singer and Malcolm 1990; Croue et al. 1999). Humic materials are preferentially removed during water treatment (Croue et al. 1999), but in waters with low humic content, hydrophilic fractions have been found to play a significant role in DBP formation (Liang and Singer 2003). Liang and Singer (2003) found that hydrophilic fractions are more reactive with bromine than hydrophobic fractions. The kinetic formation rates of DBPs are affected by the type of NOM (Croue et al. 1999, Gallard and von Guten 2002).

Disinfectant type, dose and residual concentration can affect the formation and speciation of DBPs. Free chlorine reacts with organic matter in two ways: oxidizing organics by accepting electrons from organic substrates and/or substituting into the organic matrix (Johnson and Jensen 1986). Free chlorine has a greater tendency to participate in substitution reactions than

chloramines resulting in higher halogenated DBP concentrations (Wolfe, Ward and Olson 1984; Johnson and Jensen 1986; Baribeau et al. 2000; Singer 2001; Vikesland, Pzekin and Valentine 2001). DBP formation may still occur to a limited degree when chloramines are used due to small amounts of free chlorine that may be present (Johnson and Jensen 1986), but in many cases chloramine use has decreased DBP concentrations substantially in comparison to free chlorine (Norton and LeChevallier 1997). Symons et al. (1998) found that a  $\text{Cl}_2:\text{N}$  of 5:1, by weight, produced the highest THM4 concentration while lower  $\text{Cl}_2:\text{N}$  ratios resulted in superior chloramine stability and decreased DBP formation.

Generally, temperature affects the reaction kinetics of NOM; formation kinetics increase with increasing temperature. THM formation, especially for chloroform, as well as HAA formation, have been found to be higher at warmer temperatures (Krasner et al. 1996, Singer 2001). Temperature impacts chlorinated DBP formation more than brominated DBP formation due to faster formation kinetics of the bromine substitution reactions (Krasner et al. 1996). Rodriguez et al. (2002) found that levels of THMs were higher in the summer and fall and fairly low in the winter. Dickenson, Work and Summers (2002) found that temperature affected dichloroacetic acid more than trichloroacetic acid.

THM4 concentrations increase as pH increases and HAA9 concentrations increase as pH decreases for typical water treatment pH ranges (Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Symons et al. 1996; Singer 1999; Singer 2001; Singer 2002; Liang and Singer 2003) but not all HAAs are impacted by pH the same way. Trihaloacetic acid ( $\text{X}_3\text{AA}$ ) formation decreases with increasing pH, but pH seems to have little effect on monohaloacetic ( $\text{XAA}$ ) and dihaloacetic ( $\text{X}_2\text{AA}$ ) acid formation (Stevens, Moore and Miltner 1989; Singer 1999; Singer 2002; Liang and Singer 2003).

Bromide concentration in raw water has an important effect on DBP speciation, but does not increase overall DBP concentrations (Symons et al. 1998). When bromide is present, free chlorine will rapidly oxidize bromide to hypobromous acid (HOBr); HOBr (along with residual hypochlorous acid) reacts with precursor NOM to produce bromo- and chloro-bromo substituted DBPs (Symons et al. 1996, Liang and Singer 2003). HOBr reacts faster with precursor material than HOCl resulting in faster formation of bromo- and bromo-chloro-substituted species than chloro-species (Rook 1974, Cowman and Singer 1996, Krasner et al. 1996). TOC and bromide concentrations affect overall DBP formation, but chlorine-to-bromide and bromide-to-TOC

ratios affect DBP speciation (Krasner et al. 1996, Clark et al. 2001, Liang and Singer 2003). The bromide-to-chlorine ratio changes as the applied chlorine dose changes.

### **2.2.3 Distribution System Characteristics Impacting THM and HAA Formation**

Characteristics of distribution systems contribute to changes in water quality once the water leaves the treatment plant and enters the distribution system. Most changes can be attributed to the following factors: secondary disinfectant type and residual, residence time, pipe material and diameter, and distribution system design, operation and hydraulic behavior.

Secondary disinfectant type and residual, and contact time affect the continued formation of DBPs in distribution systems. THM4 and HAA9 formation has been observed to continue as long as a free chlorine disinfectant residual is present (Meyer et al. 1993). THM4 and HAA9 formation tends to be limited in the presence of a combined chlorine residual. Hence, terminal disinfection with free chlorine has been found to produce higher DBP concentrations than terminal disinfection with chloramines (Wolfe, Ward and Olson 1984; Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Norton and LeChevallier 1997; Pope et al. 2002). Chloramines produce more chlorinated substitution products than oxidation products (Johnson and Jensen, 1986) but still produce less TOX than free chlorine. Cowman and Singer (1996) observed a 90–95% decrease in HAA9 concentrations when chloramines were utilized in comparison to free chlorine.

Federal regulations require the presence of a disinfectant residual upon entry to the distribution system. However, residuals have been shown to decay in part due to reactions with bulk-phase organics, reduced inorganics, biofilms and pipe walls (LeChevallier, Cawthon and Lee 1988b; Meyer et al. 1993; Vasconcelo et al. 1997; Chen and Wiesel 1998; Prevost et al. 1998; Lu, Kiene and Levi 1999; Baribeau et al. 2001). In order to compensate for this decay, utilities tend to increase their disinfectant dose in the treatment plant, though this may result in higher DBP concentrations. Federal regulations require the presence of a detectable disinfectant residual ( $\geq 0.2$  mg/L) in at least 95% of the samples in their distribution system monitoring program.

Contact time, or residence time, plays an important role by allowing the DBP formation reactions to continue, especially in the case of free chlorine. This tends to further consumption

of the disinfectant. Residence times within distribution systems vary, depending on the water demand patterns, distribution system network design, and in-system storage (such as reservoirs and storage tanks). DBP concentrations have been found to increase in the presence of a free chlorine residual as residence time increases (Bellar, Lichtenberg and Kroner 1974; Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Krasner et al. 1996; Baribeau et al. 2001; Singer 2001; Dickenson, Work and Summers 2002; Pope et al. 2002). Diurnal variations in water demand patterns alter contact time and can also alter observed DBP patterns. Singer (2001) reported diurnal variations of greater than 50% have been observed and attributed this to diurnal variations in water demand patterns.

Distribution system pipe material and diameter may affect DBP formation and residual decay via reactions between disinfectant residuals and pipe walls and biofilms. Reactions of disinfectant residual with pipe walls leads to a loss in residual and the production of corrosion by-products (Vasconcelos et al. 1997). Corrosion by-products aid in the formation of biofilms and create reservoirs of organic matter that may promote DBP formation.

Researchers have attempted to quantify the effect of pipe material and pipe diameter on DBP formation and residual decay by comparing kinetics of DBP formation to residual decay in bottle tests and in simulated distribution systems. The bottle tests resulted in higher residual concentrations and, as a result, higher DBP concentrations (Baribeau et al. 2001, Rossman et al. 2001). Rossman et al. (2001) found a small but consistent (15%) increase in THM4 concentrations in bottle tests versus simulated distribution system samples. As reaction time increased, no statistical difference was found in HAA production between bottle tests and simulated distribution system samples despite the lower chlorine residual in the simulated distribution system.

Disinfectant decay leading to an accumulation of corrosion by-products depends upon the pipe material and disinfectant type. Free chlorine is a stronger oxidant than chloramines and participates to a greater degree in corrosion reactions. Synthetic materials, e.g. PVC, have been found to have a very small influence on consumption of disinfectants in distribution systems, while cast iron pipes tend to have a considerable influence (Kiene, Lu and Levi 1998). PVC pipe has a much lower chlorine demand than iron pipe (LeChevallier, Lowry and Lee 1990). LeChevallier et al. (1993) found that corrosion control additives help to maintain the effectiveness and persistence of the disinfectant residual.

Surface-area-to-volume ratio of pipes has been shown to affect disinfectant decay in smaller diameter pipes; as surface-area-to-volume ratio increases, decay of disinfectant residual increases (Vasconcelos et al. 1997, Prevost et al. 1998, Baribeau et al. 2000). Baribeau et al. (2000) found that chlorine concentrations were lowest in small diameter pipes, higher in larger distribution mains, and greatest in batch contactors with the same residence time.

### **2.3 BACTERIOLOGICAL GROWTH IN THE DISTRIBUTION SYSTEM**

Biological regrowth often occurs in distribution systems, despite the presence of disinfectant residuals, and may cause a multitude of problems including an increase in disinfectant demand and corrosion rates, risk of gastrointestinal illness, and customer complaints due to taste and odor. The type of secondary disinfectant chosen and the dose applied has an impact on biological regrowth. Free chlorine has been shown to be more successful at inactivating microbial growth in the bulk liquid phase, while chloramines, which provide a more stable residual, have been shown to penetrate and inactivate biofilms more effectively (LeChevallier, Cawthon and Lee 1988b; Camper 2003). The ineffectiveness of free chlorine to inhibit biofilm growth is due to its stronger oxidation potential and its corresponding inability to penetrate the biofilm (Momba, Ndaliso and Binda 2003). Chloramines are a weaker oxidant than free chlorine; thus they react with fewer compounds in the water and biofilm matrix which improves their biofilm disinfection capabilities (LeChevallier, Cawthon and Lee 1988b). Free chlorine has a greater tendency of producing corrosion by-products as a result of interaction with the pipe wall. Attachment of bacteria to the surface of a pipe, or in tubercles and crevices, is the primary mechanism for bacterial survival against disinfection (LeChevallier, Cawthon and Lee 1988; LeChevallier et al. 1993).

HPCs are often used as an indicator of biological activity in a distribution system. However, HPCs, which usually measure suspended growth, may underestimate overall bacterial presence and biofilm thickness (Prevost et al. 1998). Suspended growth is more effectively controlled by disinfectant residuals than biofilms. Thus a reduction in HPCs does not mean that biofilms are controlled; often they are not (Camper 2003).

Utilities that chloramine may periodically switch secondary disinfectants to free chlorine in order to limit the growth of nitrifying bacteria and coliforms. However, this may lead

to increased suspended growth counts as biofilms are sloughed off the pipe wall. Zhang and DiGiano (2002) found that the switch to free chlorine in Raleigh, NC reduced the HPC, but once chloramination resumed, HPCs went back up.

Pipe material can have an impact on the regrowth and survival of biofilms. In a model pipe system, 1 mg/L residual of free chlorine or chloramines was shown to reduce viable biofilm counts one hundredfold in galvanized iron, PVC, and copper pipes (LeChevallier, Lowry and Lee 1990). Free chlorine residuals ranging from 3 to 4 mg/L were ineffective for biofilm control on iron pipes in a model distribution system; only chloramine residuals of  $>2$  mg/L were successful in reducing viable biofilm counts (LeChevallier, Lowry and Lee 1990). For copper and PVC pipe, free chlorine had greater biofilm inactivation than chloramine, whereas for galvanized iron pipe the opposite was true (LeChevallier, Lowry and Lee 1990). At least 2 mg/L of chloramine residual is needed to inactivate biofilms, though this may vary in actual distribution systems (LeChevallier, Lowry and Lee 1990). Momba, Ndaliso and Binda (2003) found colonization of stainless steel and galvanized mild steel pipes by microorganisms within 24 hours of being subjected to chlorination treatment.

Corrosion can encourage microbial regrowth in the distribution system. Free chlorine is a stronger oxidant than monochloramine and at equal concentrations is more corrosive to copper and steel (LeChevallier et al. 1993). Chloramines are more effective disinfectants in corrosive environments but, in low corrosion situations, free chlorine can inactivate biofilms on iron pipes more effectively (LeChevallier et al. 1993). Disinfection by free chlorine is affected most by pipe surface and the age of the biofilm (LeChevallier, Cawthon and Lee 1988). Biofilms that were grown for 7 days were more resistant to chlorine than 2 day-old biofilms (LeChevallier, Cawthon and Lee 1988). Disinfection by chloramines is affected most by pipe surface (LeChevallier, Cawthon and Lee 1988). The addition of phosphate-based corrosion inhibitors has been found to improve the effectiveness of free chlorine for microbial inactivation on iron pipes (LeChevallier et al. 1993; LeChevallier, Welch and Smith 1996) and has also been associated with lower coliform levels (LeChevallier, Welch and Smith 1996). pH and alkalinity adjustments have been found to increase free chlorine disinfection efficiency by reducing the corrosivity of the water (LeChevallier, Lowry and Lee 1990). Type of material (iron versus polycarbonate) and the density of corrosion deposits have been found to have more of an influence on biofilm density than chemicals used for corrosion control (Rompre et al. 2000).

LeChevallier, Welch and Smith (1996) found that temperature is the most important factor controlling microbial regrowth in drinking water. Changes in temperature affect microbial growth rates, disinfectant decay, inactivation kinetics, and corrosion rates, as well as distribution system hydraulics and water velocities due to higher water demand in warmer months. A survey of 31 utilities found that the frequency of occurrence and the density of coliform bacteria are higher when temperatures in the distribution system are above 15°C (LeChevallier, Welch and Smith 1996). The average density of coliform bacteria was 35 times higher in systems with free chlorine than in chloraminated systems; an 18-fold increase in coliform occurrence was found for systems with free chlorine when water changed from 0 to 5°C to > 20°C. A similar relationship was found for chloraminated systems, but only a 2.5-fold increase in coliform occurrence was observed (LeChevallier, Welch and Smith 1996).

A strong correlation between free chlorine residual and HPCs was found by Zhang et al (2002). As free chlorine residual increases, HPCs decrease (Prevost et al. 1998, Zhang and DiGiano 2002). HPCs have also been found to increase with an increase in residence time (Zhang and DiGiano 2002). HPCs increase more rapidly in smaller diameter pipes than larger diameter pipes (Prevost et al. 1998; Lu, Kiene and Levi 1999) because of the larger surface area.

#### **2.4 BIODEGRADATION OF HALOACETIC ACIDS**

General wisdom holds that HAA and THM concentrations increase as residence time increases for systems using free chlorine and remain relatively constant in chloraminated systems. Thus, locations of maximum concentration would be expected to be the same for each class of DBPs. However this has not proven to be the case. Loss of HAAs has been documented in full-scale distribution systems as well as on a laboratory scale (van der Ploeg, van Hall and Janssen 1991; Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995; Williams, Williams and Gordon 1996; LeBel, Benoit and Williams 1997; Chen and Wiesel 1998). Investigation of the phenomenon has uncovered several bacteria that are capable of HAA degradation, including *Xanthobacter autotrophicus GJ10* (van der Ploeg, van Hall and Janssen 1991; Williams, Williams and Yuan 1998). *Xanthobacter autotrophicus GJ10* has been shown to degrade chloroacetic acid, dichloroacetic acid, bromoacetic acid and dibromoacetic acid, but not trichloroacetic acid (van der Ploeg, van Hall and Janssen 1991; Williams, Williams and

Gordon 1995). McRae, LaPlara and Holzaski (2004) successfully cultured microorganisms of the *Sphingomonas* and *Chryso bacterium* species which are capable of degrading chloroacetic acid, bromoacetic acid and trichloroacetic acid.

HAA biodegradation occurs via enzymatic haloacid dehalogenase which is induced by dichloroacetic acid, but can be inhibited by other compounds (van der Ploeg, van Hall and Janssen 1991; Williams, Williams and Gordon 1995). The biodegradation mechanism involves displacement of the chlorine from the alpha carbon by a nucleophilic attack by water and usually results in an increase in chloride concentration and a decrease in pH (Williams, Williams and Gordon 1995). In batch experiments, chloroacetic acid was found to have biodegraded 96% from an initial concentration of 0.1 mg/L in 29 hrs and trichloroacetic acid was found to have biodegraded 44% from an initial concentration of 0.1 mg/L in 29 hrs (McRae, LaPlara and Hozalski 2004).

HAA9 biodegradation has been observed at locations with high residence times within distribution systems while THM4 concentrations consistently increase with increasing residence time (Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995; Williams, Williams and Gordon 1996; LeBel, Benoit and Williams 1997; Chen and Wiesel 1998). Locations of observed HAA9 degradation correspond to low disinfectant residuals and high HPCs (Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995). Warmer temperatures have also been correlated to HAA9 degradation (Williams, Williams and Gordon 1995; Chen and Wiesel 1998; Baribeau et al. 2000).

## **2.5 NITRIFICATION IN DISTRIBUTION SYSTEMS**

The promulgation of new DBP limits has prompted a number of utilities to change secondary disinfectants from free chlorine to chloramines. Limited additional DBP formation occurs with chloramines; however use of chloramines is not without problems. Biological nitrification can occur in distribution systems due to the presence of ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB). Typical indications of nitrification include a decrease in chloramine residual, an increase in HPCs and an increase in nitrite and nitrate concentrations (Lieu, Wolfe and Means 1993; Skadsen 1993; Odell et al. 1996; Wilczak et al. 1996; Harrington et al. 2002; Skadsen 2002; Pintar and Slawson 2003). Increases in nitrite and

nitrate concentrations as a result of nitrification have been found to be in the range of 0.05-0.5 mg/L, but can be as high as 1 mg/L (Wilczak et al. 1996). Federal regulations place a 1 mg/L limit on nitrite and a 10 mg/L limit on nitrate (USEPA, 1991). A 1996 study of utilities in the United States showed that an estimated 2/3 of medium and large utilities that chloraminate experienced nitrification, and that every fourth utility surveyed had moderate to severe nitrification problems (Wilczak et al. 1996).

AOB oxidize ammonia into nitrite and NOB oxidize nitrite into nitrate (Cunliffe 1991, Skadsen 1993, Skadsen 2002, Regan et al. 2003). While AOB and NOB populations in distribution systems have not been well characterized, common AOB genera include *Nitrosospira* and *Nitrosomonas*, and common NOB genera include *Nitrobacter* and *Nitrospira* (Cunliffe 1991, Skadsen 1993, Skadsen 2002, Regan et al. 2003). Typically, AOB exhibit slow growth, are inhibited by sunlight, and prefer conditions with pH > 8 and temperatures in the 25-30°C range, though they have been found at temperatures as low as 5°C (Skadsen 1993). AOB are capable of growing in the presence of a 1.2-1.5 mg/L disinfectant residual (Wilczak et al. 1996). If ammonia is present in concentrations that promote AOB growth and the rate of AOB growth exceeds the rate of AOB inactivation via disinfection then, theoretically, AOB growth can occur in the presence of chloramines (Harrington et al. 2002).

In addition to resistance to chloramine residual, sediment and biofilms in the distribution system may also contribute to the survival of nitrifying bacteria. Nitrifying bacteria can grow in tight cell clusters that are cyst-like and may be resistant to disinfection (Cunliffe 1991, Wilczak et al. 1996). Sediment and tubercles increase potential for nitrification (Cunliffe 1991, Odell et al. 1996). Pintar and Slawson (2003) found that fluctuations in AOB concentrations corresponded to fluctuations in chloramine residual and that chloramine residuals did not completely inhibit establishment of nitrifying bacteria. There is some indication that changes in nitrite concentrations correspond well with AOB abundance (Pintar and Slawson 2003).

Excess ammonia in treated water may encourage the growth of AOB. Common chlorine-to-ammonia ratios used in drinking water treatment range from 3:1 to 5:1, on a weight basis, but even higher ratios may not always be effective in preventing AOB growth (Wilczak et al. 1996). A chlorine-to-ammonia ratio of 3:1 leads to excess ammonia that AOB may use as substrate (Regan et al. 2003). However, several studies found that increasing the chlorine-to-ammonia

inorganic compounds have been shown to be effective in reducing nitrification (Skadsen 1993, Odell et al. 1996, Skadsen 2002).

## CHAPTER 3 MATERIALS AND METHODS

### 3.1 SELECTION OF UTILITIES

This study examined formation and decay of THMs and HAAs and associated changes in water quality in distribution systems for four utilities. Factors considered in the selection of utilities for participation in this study included: type of secondary disinfectant utilized, seasonal temperature variations, geographic location, moderate to high levels of total organic carbon (TOC) and assimilable organic carbon (AOC), presence of bromide in the raw water, evidence of microbial activity, distribution system characteristics, and distribution system modeling capabilities.

There were several criteria that were mandatory in the selection of the utilities. Utilities had to have a hydraulic model of their distribution system that could be used to determine residence time for the selection of sampling locations in the distribution system. In addition, simple and well-characterized networks were preferred in order to maximize control over the factors that contribute to changes in water quality. Treated water could not be blended (e.g. with groundwater) so that identification of the factors affecting DBP formation, speciation and decay would be less complex. Minimum levels of DBPs, THM4 > 40 µg/L and HAA9 > 20 µg/L, were also required for participation.

Samples taken from the distribution system were analyzed for disinfectant residual, TOC and AOC concentrations, ultraviolet (UV) absorbance, ammonia, nitrite, nitrate, HPCs, THMs and HAAs. Utilities were sampled over a 15-month period, beginning in August 2002 and ending in October 2003. Each utility was sampled 6–8 times throughout the sampling period. Descriptive data for the chosen utilities is presented in Chapter 4.

### 3.2 SELECTION OF SAMPLING LOCATIONS

Selection of sampling locations for each utility was based on several criteria. For each utility, a range of residence times was chosen to represent extremes of each distribution system. Hydraulic models were used to determine residence times. In addition to residence time,

pressure zones, booster chlorination and storage reservoirs were also considered in picking sampling locations. Sampling locations within the same pressure zone and outside flushing zones were preferable. If a system contained booster chlorination and/or storage reservoirs, sampling locations were chosen before and after each entity.

Pipe material and diameter were also considered in selection of the sampling locations. Sampling locations were chosen to represent various materials and diameters found throughout a given distribution system, including mains and small distribution lines. Additionally, critical areas of importance, such as locations of low or non-measurable disinfectant residual and locations with microbiological and/or nitrification occurrence, were also considered.

Sampling locations for the chosen utilities are presented in Chapter 4.

### **3.3 GLASSWARE AND BOTTLE PREPARATION**

Forty mL glass sampling vials with screw caps and PTFE-faced septa were used for collecting samples. The vials were used for THM, HAA, UV and TOC samples and were cleaned and prepared by the University of North Carolina (UNC) and the Newport News Waterworks (NNWW). Five hundred mL AOC bottles and 20 mL HPC vials were cleaned and prepared by the American Water Works Service Company (AWWSC). Sample bottles for ammonia, nitrite and nitrate for use by Utility C were cleaned and prepared by the NNWW. Utility D, which also measured ammonia, nitrite and nitrate, utilized several HACH methods which are summarized in Table 3.1.

Sample vials utilized for DBP analysis were prepared by soaking the 40 mL vials overnight in a bath of tap water and detergent (Alconox, Inc, White Plains, NY), rinsing three times with laboratory grade water (Dracor, Durham, NC), immersing the vials overnight in a 10% nitric acid bath (Fisher Chemicals, Fair Lawn, NJ), rinsing three times with laboratory grade water, rinsing three times with methanol (Mallinckrodt Chemicals, Phillipsburg, NJ) and oven-drying for 24 hours at 180°C. All field blank and batch test bottles were prepared in the same manner. Plastic screw caps and PTFE-lined silicone septa (Laboratory Supply Distributors Corp., Mt Laurel, NJ) were soaked overnight in a tap water and detergent bath, rinsed three times with laboratory grade water, rinsed three times with methanol, and left to dry in a hood for several hours.

Glassware used to analyze TOC was rinsed three times with tap water, soaked overnight in a 10% nitric acid bath, rinsed three times with tap water, rinsed three times with laboratory grade water and oven-dried overnight at 180°C.

UV and TOC vials were not prepared with preservatives. THM and HAA sample vials contained preservatives according to standard operating procedures. Approximately 20 mg of ammonium sulfate (Mallinckrodt Chemicals, Paris, KY) and 0.7 g of phosphate buffer were added after cleaning and prior to shipment to preserve THMs and to standardize the pH of all the THM samples between 4.8 and 5.5 upon sample collection. Fifty µL of an 80 mg/L sodium azide (Sigma Aldrich, Milwaukee, WI) solution and 20 mg of ammonium sulfate were added after cleaning and prior to shipment to preserve HAAs and prevent microbial growth upon sample collection.

### 3.4 SAMPLING PROTOCOL

Sample vials for THMs, HAAs, UV absorbance and TOC prepared by UNC and NNWW were sent to the appropriate utilities prior to the sampling date. AOC and HPC vials prepared by AWWSC were shipped to the appropriate utilities prior to the sampling date. Utility D, which also measured free ammonia, total ammonia, nitrite and nitrate, utilized several HACH methods, which are summarized in Table 3.1, and followed HACH protocol.

On the morning of sampling, all vials were placed in coolers with frozen ice packs. At a given sampling location, the faucet, hydrant, or other water spigot was turned on and allowed to run for five minutes, if it was not already running continuously. After five minutes, chlorine, temperature and pH measurements were made. All vials were filled such that sample water ran down the sides of the vials and were filled headspace-free to prevent volatilization of DBPs. A duplicate sample was collected. Samples were stored in coolers containing frozen ice packs. One field blank was prepared at a randomly selected site for each utility. Field blanks consisted of filling an empty 40-mL vial with laboratory grade water that was sent to the utility, and were used to determine if contamination had occurred during sampling or storage. Upon completion of sampling, all samples were shipped by overnight carrier to the appropriate laboratory on the day of sampling. Upon receipt, samples were stored at 4°C until analyzed. THM, HAA, UV and

TOC samples were sent to UNC and NNWW. AOC and HPC samples were sent to AWWSC. Analyses performed by each laboratory and utility are summarized in Table 3.1.

Table 3.1  
Matrix of analyses conducted

Parameters	Laboratory						Utilities	
	UNC		NNWW		AWWSCo		Method	Utilities
	Method	Utilities	Method	Utilities	Method	Utilities		
Temperature							On-site	A B C D
pH							On-site	A B C D
Free and Total Chlorine Residual							On-site (colorimetry, adapted from APHA, 1998)	A B C D
Free and Total Ammonia			EPA Method 350.1 (USEPA, 1978b)‡	C			HACH Method 8155 for DR-890*	D
Nitrite			EPA Method 353.2 (USEPA, 1978a)	C			HACH Method 8507 for DR-890 (USEPA, 1979)	D
Nitrate			EPA Method 353.2 (USEPA, 1978a)	C			EPA Method 300.0 (USEPA, 1993)	D
UV <sub>254 nm</sub>	SM 5910 B with modifications	A D	SM 5910 B with modifications	C B				
TOC	SM 5310 B	A D	SM 5310 B	C B				
Bromide			EPA 300.1	C			EPA 300.1	D
THM4	SM 6232 B	A D	EPA Method 502.2 (USEPA, 1989)	C B				
HAA9	SM 6251 B with modifications	A D	EPA Method 552.2 (USEPA, 1992)	C B				
HPC			SM 9215 D	C	SM 9215 B			A B D
AOC					LeChevallier et al (1993)		All utilities	

UNC: University of North Carolina; NNWW: Newport News Waterworks; AWWSCo: American Water Works Service Company, Inc.; Utility D

SM: Standard Method (APHA 1998)

\*: Total ammonia only (salicylate method adapted from Clin. Chim. Acta., 14:403, 1966); †: Free ammonia only;

‡: Total ammonia.

### 3.5 ANALYTICAL PROCEDURES

The analytical procedures described in this section for TOC, UV absorbance, THMs and HAAs were performed at the UNC laboratories for samples collected from the distribution systems of Utilities A and D. NNWW performed the same analyses for Utilities B and C. Utility D analyzed ammonia, nitrite and nitrate samples taken from their distribution system, and NNWW analyzed ammonia, nitrite and nitrate samples taken from Utility C's distribution system. AWWSCo. analyzed HPC samples from Utilities A, B and D, as well as AOC samples taken from all the distribution systems. HPC samples collected from Utility C were analyzed by NNWW. Chlorine residual, temperature and pH measurements were made on-site at the time of sample collection. Samples were removed from refrigeration one hour prior to analysis to allow the samples to come to room temperature.

#### 3.5.1 Total Organic Carbon (TOC)

TOC was measured following a slightly modified Standard Method 5310B (Standard Methods, 1998) using a Shimadzu 5000 Total Organic Carbon Analyzer (Shimadzu Corporation, Norcross, GA) equipped with an ASI auto-sampler. One modification was employed: hydrochloric acid (Fisher Scientific, Fairlawn, NJ) was used for acidification of samples instead of phosphoric acid because the Shimadzu 5000 analyzer is sensitive to excess phosphoric acid.

Four calibration points were developed each time the analyzer was run. Calibration points ranged from 0 to 6 mg/L of TOC. Dilutions were made from a 1000 mg/L TOC standard. A new standard was made every month by adding 2.128 g of potassium hydrogen phthalate (Fisher Scientific, Fairlawn, NJ) to 1000 mL of laboratory grade water.

Prior to loading the samples, a mechanical check was performed on the analyzer. Ultra-high purity air (Holox Company, Morrisville, NC) was utilized as the carrier gas. TOC vials were rinsed with laboratory grade water, rinsed with a small amount of sample and then filled with sample to 90% capacity. Three drops of hydrochloric acid were added to samples and five drops were added to calibration standards. Duplicate analyses were run for all samples and were checked if there was more than a 10% variation, except in cases when there was no second

sample available. A calibration check point was added after every ten samples and the full calibration curve was run after all the samples had been analyzed to provide quality control.

### **3.5.2 Ultraviolet (UV) Absorbance**

UV absorbance was measured at 254 nanometers (nm) following Standard Method 5910B (Standard Methods, 1998) on a U-2000 UV-Visible spectrophotometer (Hitachi Instruments, Danbury, CT). A 5-cm cell was used to measure UV absorbance values. The spectrophotometer was zeroed with laboratory grade water prior to measuring UV absorbance of the samples. Before transferring a sample aliquot to the 5 cm cell, the cell was rinsed with laboratory grade water, rinsed with a small amount of sample and then filled with sample. Care was taken to ensure no air bubbles were attached to the walls of the cell. Duplicate analyses were run for all samples to assure that there was less than 10% variation, except in cases when there was no second sample available. A check with laboratory grade water was performed after every ten samples.

### **3.5.3 Trihalomethanes (THM4)**

#### *3.5.3.1 Analytical Procedure*

Forty mL samples were collected in duplicate from the utility distribution systems and analyzed for all four THMs: chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ) and bromoform ( $\text{CHBr}_3$ ). All samples were extracted within two weeks of collection. THMs were extracted via liquid-liquid solvent extraction based on EPA Method 551.1 (USEPA 1995) and Standard Method 6232B (Standard Methods 1998) procedures with minor modifications. THM extraction and analysis was conducted according to the standard operating procedures in our laboratory, which are available upon request.

A 25 mL graduated cylinder was used to measure a 20-mL aliquot of the 40 mL sample. The rest of the sample was discarded and the 20 mL aliquot was returned to the 40 mL vial. Before measuring out the next 20 mL aliquot of sample, the graduated cylinder was rinsed three times with laboratory grade water and once with a small amount of the next sample. Four mL of

methyl-*tert*-butyl ether (MtBE, Sigma Aldrich, Milwaukee, WI) containing 100 µg/L of 1,2 dibromopropane (Sigma Aldrich, Milwaukee, WI) was added to the 20 mL aliquot. The 1,2 dibromopropane served as an internal standard (IS) to correct for changes in sample injection volume. Six g of sodium sulfate (Mallinckrodt, Paris, KY), which had been baked at 400 °C for 24 hours to remove organics, was added to the 20 mL aliquot to aid in the extraction of the THMs into the MtBE. The sample was then vortex-mixed (Type 16700 Mixer-MaxiMix I, Thermolyne, Dubuque, IA) for one minute. The samples were left to sit at least five minutes so that the sodium sulfate crystals could settle to the bottom of the vial and the solvent layer could separate. One mL or more of the MtBE layer was transferred by Pasteur pipette to a 2 mL glass autosampler vial (Laboratory Supply Distributors, Mt. Laurel, NJ) and capped with an aluminum PTFE-faced seal (Laboratory Supply Distributors, Mt. Laurel, NJ). During the first few analyses, samples were double-vialed in case re-analysis was required. Both sets of samples were stored in a laboratory freezer at -15°C until analysis by gas chromatography.

A calibration curve was created for each set of samples processed. THM4 stock standards (5000 µg/mL of each analyte, Supelco, Bellefonte, PA) were diluted several times in methanol and two calibration standards were created. Standard 1 was comprised of 100 µg/mL of CHCl<sub>3</sub>, 50 µg/mL of CHBrCl<sub>2</sub> and CHBr<sub>2</sub>Cl, each, and 20 µg/mL of CHBr<sub>3</sub>. Standard 2 was comprised of 4 µg/mL of CHCl<sub>3</sub>, 2 µg/mL of CHBrCl<sub>2</sub> and CHBr<sub>2</sub>Cl, each, and 0.8 µg/mL of CHBr<sub>3</sub>. Calibration points were prepared with Standards 1 or 2 and laboratory grade water. Table 3.2 illustrates the calibration points used for all sampling locations.

Table 3.2

THM species concentration for eight calibration points

Level	Concentration (µg/L)			
	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>
1	0.0	0.0	0.0	0.0
2	1.0	0.5	0.5	0.2
3	5.0	2.5	2.5	1.0
4	10	5.0	5.0	2.0
5	25	12.5	12.5	5.0
6	50	25	25	10
7	100	50	50	20
8	250	125	125	50

Separation, identification and quantification of THMs occurred via gas chromatography (GC) with electron capture detection (ECD) on a Hewlett Packard GC 5890A with an autosampler/autoinject tower and a Hewlett Packard Model ECD (Hewlett-Packard Company, Cary, NC), respectively. Operating conditions for the GC/ECD are presented in Table 3.3. Chromatograms generated for the calibration points were used to identify the retention time for the THM species and the internal standard. The area under each of the peaks was integrated, a ratio was computed for each of the THM species relative to the internal standard, and a calibration curve for the relative area of the standards was prepared. All calibration points were created in duplicate. The concentration of each THM species was determined by comparing the relative area of the sample to the relative area of the standards using the calibration curve. An algorithm established in Microsoft Excel was used to generate the calibration curve and compute sample concentrations.

Table 3.3

Gas Chromatographic conditions for analysis of THMs

Temperature Sequence:	Initial Temperature:	35 °C, hold for 10 mins
	Level 1:	150 °C at a rate of 10 °C/min
	Level 2:	250 at a rate of 25 °C/min; hold for 11 mins
Injector:	Sample volume:	2 µg/L
	Rinse Solvent:	MtBE
	Temperature:	150 °C
Detector:	Type:	Electron capture
	Temperature:	300 °C
Gas:	Carrier:	Ultra high purity nitrogen (HoloX Company, Morrisville, NC)
	Make up:	Ultra high purity nitrogen (HoloX Company, Morrisville, NC)
Total run time:		36.5 mins

### 3.5.3.2 *Quality Assurance and Quality Control*

Reagents and calibration standards were run on the GC prior to their use to determine that no contamination or degradation had occurred. All new batches of MtBE, along with a sample of MtBE plus IS, were also run on the GC prior to use. THM species stock standards were discarded and replaced every six months regardless of contamination or degradation. Test mixes of both Standards 1 and 2 were generated prior to use and run on the GC to determine if degradation or contamination had occurred. If degradation of more than 20% had occurred, the standard was discarded and replaced. Regardless of contamination or degradation, Standards 1 and 2 were discarded every two months and new standards were made.

Check standards and matrix spikes were utilized to measure the applicability of the calibration curve and to ensure good quantification of the analytes by the GC. Check standards of calibration points were analyzed after every eight samples. A sample of MtBE plus IS was injected before and after the check standard to ensure that carry-over did not occur. Matrix spikes were used to determine the recovery of individual THM species. Two sets of matrix spikes were prepared for each set of samples. All samples were extracted in duplicate unless there was no duplicate available. Sample data was checked for reproducibility of plus or minus 20%. An average of the duplicates was reported. In some cases, inconsistencies were found between a sample and its duplicate due to issues with the IS. When this occurred, only the value deemed to be correct was reported. The minimum reporting level (MRL) for all species was 1 µg/L. Any sample data point that was below the MRL was reported as < 1 µg/L.

## 3.5.4 **Haloacetic Acids (HAA9)**

### 3.5.4.1 *Analytical Procedure*

Samples collected from the utility distribution systems were analyzed for all nine HAAs: trichloroacetic acid (Cl<sub>3</sub>AA), tribromoacetic acid (Br<sub>3</sub>AA), bromodichloroacetic acid (BrCl<sub>2</sub>AA), dibromochloroacetic acid (Br<sub>2</sub>ClAA), dichloroacetic acid (Cl<sub>2</sub>AA), dibromoacetic acid (Br<sub>2</sub>AA), bromochloroacetic acid (BrClAA), monochloroacetic acid (ClAA) and monobromoacetic acid (BrAA). HAAs were extracted using the micro liquid-liquid extraction procedure based on Standard Method 6251B (Standard Methods 1998) and U.S. EPA Method 552 (USEPA 1995)

with minor variation (Brophy, Wienberg and Singer, 2000). HAA extraction and analysis was conducted according to the standard operating procedures in our laboratory, which are available upon request.

Diazomethane was generated and captured by collecting the diazomethane vapor in MtBE. One 40 mL glass vial, Vial 1, was connected to another 40 mL glass vial, Vial 2, by PTFE tubing, with an inner diameter of 0.8 mm. The tubing was connected to each vial via open-top screw caps which were mounted with PTFE-lined silicone septa. Small holes had been drilled in each septum and the tubing was inserted in each hole. A vent was also placed through the septum of Vial 1. Ten mL of MtBE (Sigma Aldrich, Milwaukee, WI) was poured into Vial 1 and the tubing was immersed in the MtBE. Vial 1 was then placed in an ice-water bath.

Reagent 1, comprised of 3.3 g of Diazald (Sigma Aldrich, Milwaukee, WI), 5 mL of Carbitol (Sigma Aldrich, Milwaukee, WI) and 5 mL of MtBE, was produced in a third 40 mL vial, capped with a screw top and PTFE-lined silicone septum, and gently swirled. Reagent 2, comprised of 6 mL of laboratory grade water, 10 mL of high purity methanol, and 4 mL of potassium hydroxide was produced in a fourth 40 mL vial, capped with a screw top and PTFE-lined silicone septum, and gently swirled.

Six mL of Reagent 1 and 6 mL of Reagent 2 were combined in Vial 2 and quickly capped to capture the diazomethane gas. Care was taken to ensure that the end of the tubing was not immersed in the liquid. The gas traveled through the tubing to Vial 1 and was trapped in the MtBE. Once the MtBE turned a dark yellow color, Vial 1 was quickly capped with a new screw cap and PTFE-lined silicone septum, placed in a double-walled bomb and stored in an explosion-proof freezer. Glassware utilized in the generation of the diazomethane was soaked in a 5 N sodium hydroxide bath for a minimum of 24 hours, rinsed with tap water, rinsed three times with laboratory grade water, and rinsed once with methanol.

Samples were stored at 4°C for no longer than three weeks from collection. A 25 mL graduated cylinder was used to measure a 20 mL aliquot of the 40 mL sample. The rest of the sample was discarded and the 20 mL aliquot returned to the 40 mL vial. Before measuring out the next 20 mL aliquot of sample, the graduated cylinder was rinsed three times with laboratory grade water and once with a small amount of the next sample.

Each 20 mL aliquot of sample received 20 µL of 2,3 dibromopropionic acid (Supelco, Bellefonte, PA) followed by 1.5 mL of sulfuric acid. The 2,3 dibromopropionic acid served as

an acid surrogate to assess the derivatization efficiency. The addition of the sulfuric acid heated the samples; thus the samples were placed on ice until they reached room temperature. Four mL of MtBE plus IS (1,2 dibromopropane) was added to each sample. Approximately 10 g of sodium sulfate (Mallinckrodt, KY), baked at 400 °C for 24 hours, was added to each sample and each sample was vortex-mixed (Type 16700 Mixer-MaxiMix 1, Thermolyne, Dubuque, IA) for one minute. Two mL of the MtBE layer was transferred to a 2 mL volumetric flask by a Pasteur pipette. Each flask was capped with a screw cap and PTFE-lined silicone septum. Approximately half of a small rounded scoop of anhydrous, magnesium sulfate (Sigma Aldrich, Milwaukee, WI) was added to each volumetric flask to absorb any water that might affect the derivatization process. Samples extracted at the beginning of the study were dosed with 225 µL of diazomethane; samples extracted near the end of the study were dosed with 200 µL of diazomethane due to replacement of the micropipetter. Samples were refrigerated for 15 minutes and checked for a yellow color upon removal from the refrigerator. Presence of the yellow color indicated that sufficient diazomethane was present to drive the esterification process. Samples were allowed to warm to room temperature after which a small rounded scoop of silicic acid (J.T. Baker, Phillipsburg, NJ) was added to the samples. Approximately 1 mL of sample was transferred using a Pasteur pipette to a glass GC vial and crimped with an aluminum TFE cap. Extracted samples were stored at -15°C until analysis by the GC (Hewlett-Packard Company, Cary, NC). Operating conditions for the GC/ECD are presented in Table 3.4. Extracted samples were run on the GC and quantified in the same manner as the THMs, presented in Section 3.6.3.1, except for the differences in temperature and injector settings.

Table 3.4

Gas Chromatographic conditions for analysis of HAAs

Temperature	Initial Temperature:	37 °C, hold for 21 mins
Sequence:	Level 1:	136 °C at a rate of 5 °C/min, hold for 3 mins
	Level 2:	250 °C at a rate of 20 °C/min; hold for 3 mins
Injector:	Sample volume:	1 µg/L
	Rinse Solvent:	MtBE
	Temperature:	180 °C
Total run time:	52.5 mins	

A calibration curve was created for each set of samples processed. Calibration points were prepared by using an HAA9 calibration standard and laboratory grade water. Six calibration points were prepared and are presented in Table 3.5. The calibration standard was prepared from an HAA6 stock standard (EPA 552 Halogenated Acetic Acids Mix, Supelco, Bellefonte, PA) containing 2000 µg/mL each of ClAA, BrAA, Br<sub>2</sub>AA, Cl<sub>2</sub>AA, BrClAA and Cl<sub>3</sub>AA and individual stock standards of Br<sub>2</sub>ClAA, Cl<sub>2</sub>BrAA and Br<sub>3</sub>AA with concentrations of 1000 µg/mL (Supelco, Bellefonte, PA). During the early phases of the study, calibration point 5 contained 25 µg/L of each analyte; however, due to a change in the micropipetter, calibration point 5 was changed and contained 24 µg/L of each analyte. The HAA9 standard was prepared with MtBE at a concentration of 20 µg/ml of each HAA species and stored in an amber vial with a screw-top and PTFE-lined silicone septum.

Table 3.5  
HAA species concentration for six calibration points

Level	Concentration (µg/L)								
	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
3	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
4	10	10	10	10	10	10	10	10	10
5	25	25	25	25	25	25	25	25	25
6	50	50	50	50	50	50	50	50	50

#### 3.5.4.2 Quality Assurance and Quality Control

Quality assurance and quality control procedures (check standards, matrix spikes, extraction in duplicate, reporting of average concentrations, etc.) utilized in analyzing the HAA9 data were the same as those utilized in analyzing the THM4 data, and are described in Section 3.6.3.2, with a few exceptions. The Br<sub>3</sub>AA stock standard was discarded and replaced every 4 months and the Br<sub>2</sub>ClAA and Cl<sub>2</sub>BrAA stock standards were discarded and replaced every 5 months. The HAA9 standard was replaced every month regardless of degradation. The MRL was 2 µg/L for all HAA species. Any sample data point that was below the MRL was reported as < 2 µg/L.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 UTILITY C

Utility C is located in the southeastern portion of the United States. Water used for drinking water is primarily surface water, occasionally supplemented by groundwater. Utility C utilizes chloramines as a secondary disinfectant, with no booster chlorination within the distribution system and no periodic switch to free chlorine. Utility C was sampled 8 times from October, 2002 through October, 2003.

##### 4.1.1 Distribution System Sampling Locations

Utility C utilizes H2ONET for hydraulic modeling of their distribution system. The model was calibrated with field measurements of hydraulic gradelines and system pressures against values predicted by the model. Thirteen sampling locations were selected to represent a cross-section of residence times found in the distribution system. Average, minimum, and maximum residence times were obtained for each sampling location by running the model at average yearly flow conditions.

Table 4.1 illustrates residence time results obtained from the model, as well as pipe material and pipe diameter data for each sampling location. Average residence times ranged from 0 to 120 hours. The pipe material is the same for all sampling locations. Pipe diameters ranged from 6 to 14 inches.

Table 4.1  
Sample site characteristics for Utility C

Sample ID	Pipe Diameter (in.)	Pipe Material	Residence Time (hrs)		
			Min	Avg	Max
POE			0	0	0
1	14	UCI**	9	6	1
2	8	UCI	41	24	4
3	12	UCI	45	32	3
4	8	UCI	64	43	38
8	8	UCI	52	39	10
9	6	UCI	49	32	7
10	8	UCI	32	21	2
13	10	UCI	2	11	16
20	8	UCI	11	8	3
15	8	UCI		>120*	
1721	10	UCI		24*	

\* Estimated water ages based on the location of these stations and the map of water age contours

\*\* UCI Unlined Cast Iron

#### 4.1.2 Distribution System Sampling Results

Tables 4.2 through 4.5 present temperature, pH, chlorine residual, organic carbon, HPC, nitrogen, THM4 and HAA9 data for Utility C for sampling date 10/21/03. Data for the other sampling dates are presented in Appendix A. Samples were taken to measure AOC at the point of entry only. TOC and ultraviolet absorbance (UV254) were measured at all sampling locations for all sampling dates. Treated water AOC concentrations were moderate and ranged from 211 to 421  $\mu\text{g/L}$  for all sampling dates. Point of entry TOC concentrations ranged from 2.53 to 3.31 mg/L and fluctuated within the distribution system between 2.12 and 3.35 mg/L. UV254 values ranged from 0.048 to 0.064  $\text{cm}^{-1}$  at the point of entry and from 0.028 to 0.067  $\text{cm}^{-1}$  in the distribution system.

Temperature and pH were measured at all sampling locations for all sampling dates. pH values at the point of entry ranged from 6.98 to 7.59 and from 6.64 to 8.67 within the distribution system. Distribution system temperatures ranged from 9.0 to 28.0°C. Distribution system

temperatures decreased during the winter months and increased during the summer months, as expected.

Table 4.2  
pH, temperature and chlorine data for Utility C for 10/21/03

Sample ID	Temperature (°C)	pH	Total Cl <sub>2</sub> (mg/L)
POE	19	7.4	4.0
1	19	7.5	3.6
2	20	7.5	3.1
3	21	7.8	3.7
4	20	7.7	3.6
8	21	7.7	3.6
9	21	7.8	3.5
10	21	7.8	3.3
13	21	7.9	3.9
20	22	7.8	0.9
15	21	7.8	0.04
1721	22	7.9	2.3

Table 4.3  
Organic carbon, microbiological and nitrogen data for Utility C for 10/21/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE	211	3.19	0.060	0.0E+00	0.718	2.41	0.062
1		3.16	0.067	1.0E+00	0.708	2.04	0.048
2		3.19	0.063	1.0E+01	0.777	4.45	0.065
3		3.18	0.063	2.0E+00	0.725	7.53	0.083
4		3.25	0.064	4.0E+00	0.793	4.56	0.082
8		3.16	0.066	4.0E+00	0.725	2.99	0.066
9		3.17	0.060	3.0E+00	0.729	2.26	0.070
10		3.16	0.065	6.0E+00	0.746	2.59	0.065
13		3.16	0.065	2.0E+00	0.743	2.9	0.087
20		3.11	0.051	1.1E+02	0.585	140.1	0.416
15		2.91	0.048	1.1E+04	0.033	<0.50	0.928
1721		3.16	0.060	1.2E+01	0.672	8.63	0.110

Table 4.4

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility C for 10/21/03

Sample ID	$\text{CHCl}_3$	$\text{BrCl}_2\text{CH}$	$\text{Br}_2\text{ClCH}$	$\text{CHBr}_3$	THM4
POE	55	14	3	<1	72
1	56	17	4	<1	77
2	52	17	4	<1	73
3	58	20	4	<1	82
4	58	18	4	<1	80
8	55	19	4	<1	78
9	50	17	4	<1	71
10	53	18	4	<1	75
13	56	17	4	<1	77
20	54	18	4	<1	76
15	55	18	4	<1	77
1721	54	18	4	<1	76

Table 4.5

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility C for 10/21/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
POE	4	7	19	4	1	19	5	2	<1	61
1	<2	8	20	4	1	18	5	2	<1	58
2	<2	10	26	5	1	19	6	2	<1	69
3	<2	11	33	7	2	19	7	3	<1	82
4	<2	8	21	5	1	19	5	2	<1	61
8	<2	8	24	5	1	19	6	2	<1	65
9	<2	7	21	4	1	18	5	2	<1	58
10	<2	8	17	4	1	15	4	2	<1	51
13	<2	10	28	5	1	27	7	2	<1	80
20	<2	3	19	5	1	26	5	2	<1	61
15	<2	2	4	<1	<1	4	2	<1	<1	12
1721	<2	10	31	6	2	21	7	2	<1	79

### 4.1.3 Total Chlorine Residual

The average total chlorine residual measured at the point of entry for all sampling dates was 3.7 mg/L, with a range of 3.3–4.0 mg/L. Total chlorine residual information for the point of entry was not available for sampling date 2/25/03. The total chlorine concentration consisted primarily of combined chlorine, i.e. monochloramine; free chlorine concentrations were not measured. Figure 4.1 illustrates the relationship between residence time and total chlorine residual in Utility C's distribution system for samples taken on 10/21/03. Corresponding figures for the other sampling dates are presented in Appendix A. The literature review in Chapter 2 indicates that one benefit of using chloramines is the stability of the residual throughout the distribution system (Wolfe, Ward and Olson 1984; Vikesland, Pzekin and Valentine 2001). At several sampling locations, the total chlorine residual decreased significantly. In particular, a loss in total chlorine residual occurred at sampling locations 20, 1721 and 15 (residence times of 8, 24 and >120 hours, respectively); this trend was observed for all of the sampling dates. For five out of the eight sampling dates, location 15 (residence time > 120 hours) had less than 0.5 mg/L of total chlorine residual. All of the sampling locations are located on unlined cast iron pipe, which may contribute to the loss of total chlorine residual, especially in small-diameter pipes (Kiene, Lu and Levi 1998). Loss of total chlorine residual appears to be correlated more with residence time and specific conditions at the sampling locations, than with seasonal changes in temperature.

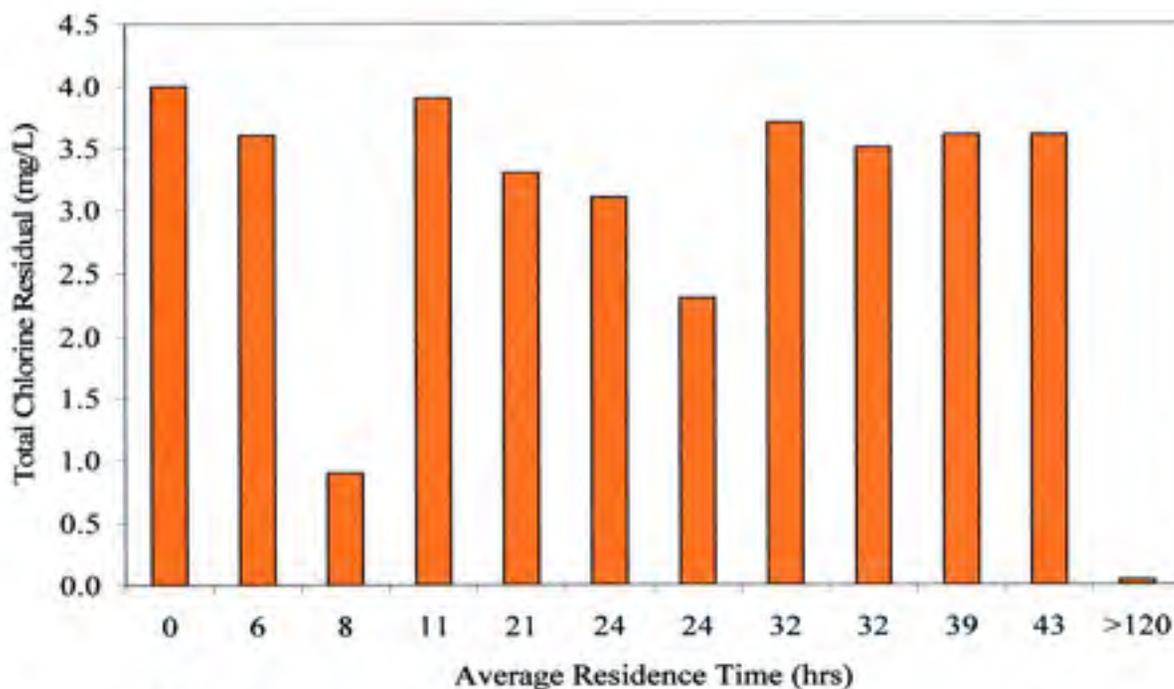


Figure 4.1 Total chlorine residual versus average residence time for Utility C for 10/21/03

#### 4.1.4 Heterotrophic Plate Counts

Figure 4.2 presents changes in HPC and total chlorine residual as residence time increases. Corresponding figures for the other sampling dates are presented in Appendix A. Increases in HPCs tended to occur at the same sampling locations as loss in total chlorine residual. Sampling location 15 (residence times >120 hours) typically had higher HPCs than the other sampling locations. HPCs for all sampling dates were less than 1000 CFU/mL, except for sampling location 15 (residence time >120 hours). Location 15 consistently had HPCs greater than 1000 CFU/mL, except for sampling date 2/25/03 when the HPC fell below 100 CFU/mL. In addition, on sampling date 10/15/02, sampling location 15 (residence time >120 hours) had a total chlorine residual of 2.2 mg/L but still had an HPC above 1000 CFU/mL. Decreases in total chlorine residual and increases in HPCs were also seen for location 20 (residence time of 8 hours). This trend is unusual due to the short residence time at this location and there is no clear reason as to why this occurs. It is possible that the residence time at location 20 is not really 8 hours and that the hydraulic model gives an erroneous value for this location. LeChevallier, Lowry and Lee (1990) found that, for iron pipes, a monochloramine residual of greater than 2

mg/L is needed to control microbial activity. HPCs tended to decrease as water temperatures decreased and increased slightly as distribution system temperatures increased.

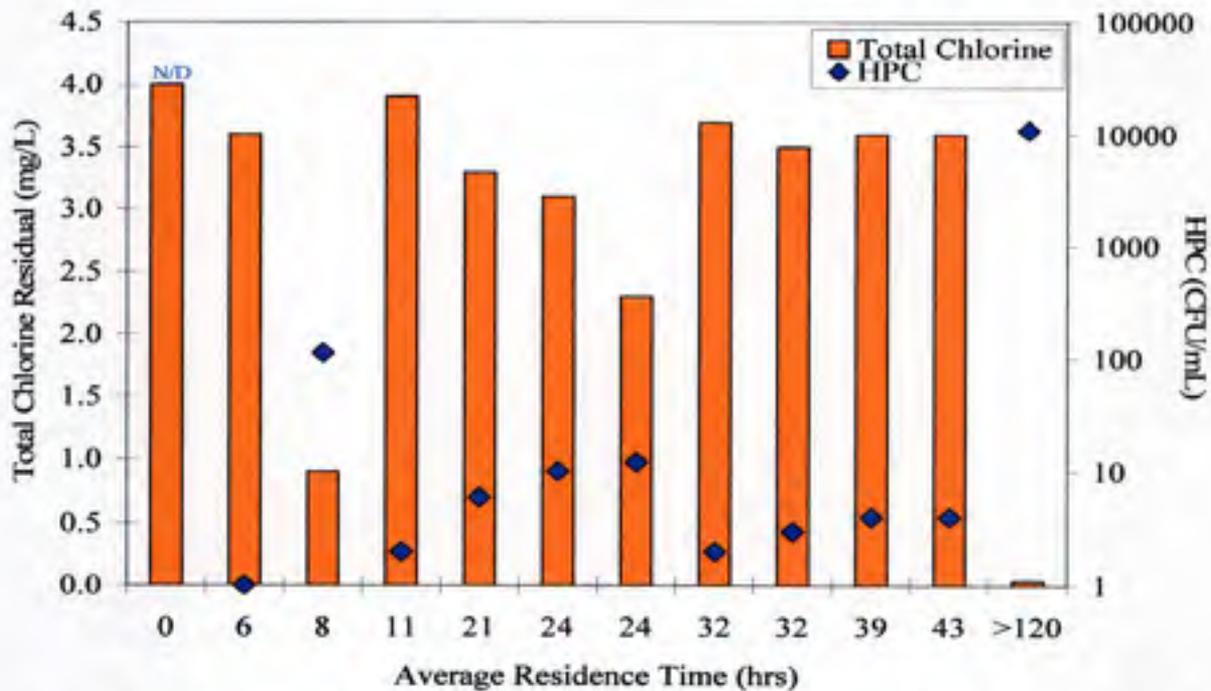


Figure 4.2 Total chlorine residual and HPCs versus average residence time for Utility C for 10/21/03

#### 4.1.5 Disinfection By-Product Formation

Figure 4.3 presents average THM4 and HAA9 concentrations and total chlorine residual as residence time increases for sampling conducted on 10/21/03. Corresponding figures for the other sampling dates are presented in Appendix A. THM4 concentrations are relatively stable as residence time increases, despite the loss in total chlorine residual; this trend was found for all sampling dates. This pattern is consistent with the literature (Johnson and Jensen 1986, Norton and LeChevallier 1997). In spite of the frequent loss in total chlorine residual at sampling location 15 (residence time >120 hours), THM4 concentrations remained consistent with those found in other parts of the distribution system. THM4 concentrations decreased as water temperatures decreased during colder months and increased as water temperatures increased

during warmer months. During the warmer months, several locations exceeded the MCL for THM4 of 80  $\mu\text{g/L}$ .

Utility C was experiencing drought conditions when sampling began in October, 2002. As a result, bromide concentrations in the raw water were higher than normal. Results from the first two sampling dates, 10/15/02 and 11/18/02 (see Appendix A), indicate that the treated water contained bromoform ( $\text{CHBr}_3$ ) and substantial concentrations of dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ). Subsequent samplings were dominated by chloroform ( $\text{CHCl}_3$ ) and bromodichloromethane ( $\text{CHBrCl}_2$ ). Although THM4 concentrations on 10/15/02 were comprised of appreciable amounts of bromine-containing compounds, the overall THM4 concentrations were lower than THM4 concentrations measured one year later on 10/21/03 (despite higher distribution system temperatures on 10/15/02). This may be attributed to the fact that TOC concentrations were higher on 10/21/03 than on 10/15/02.

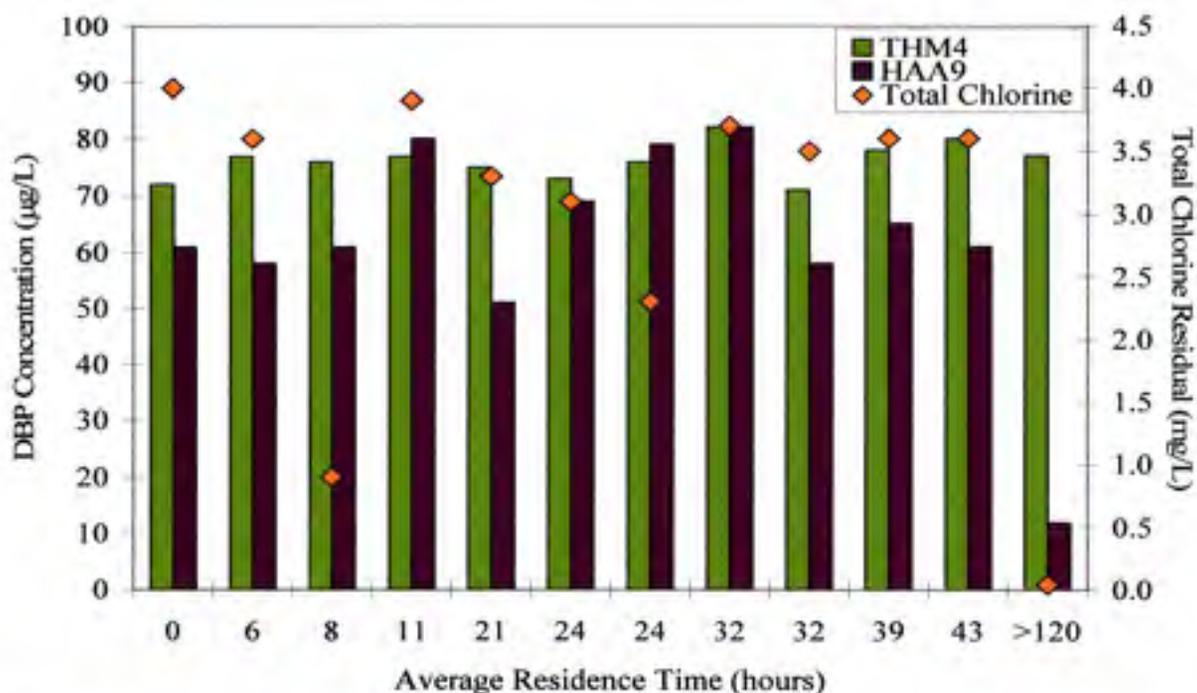


Figure 4.3 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 10/21/03

Figure 4.3 also presents average HAA9 concentrations as residence time increases for sampling conducted on 10/21/03. Unlike the THM4 concentrations, the HAA9 concentrations

are more variable throughout the distribution system, a phenomenon found for all sampling dates. Variations in HAA9 concentration do not seem to follow a discernable pattern, with the exception of sampling location 15 (residence time >120 hours), where a marked decrease in HAA9 concentrations occurred for six out of eight sampling dates. Location 15 (residence time >120 hours) consistently had low total chlorine residuals and the highest HPCs of all sampling locations. The presence of elevated HPCs and the loss in disinfectant residual at this high residence time location suggests that biodegradation of HAA9 is responsible for the observed decrease in HAA9 concentrations. These conditions are consistent with those found to promote biodegradation of HAA9 (Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995; Williams, Williams and Gordon 1996; LeBel, Benoit and Williams 1997; Chen and Wiesel 1998). Generally, HAA9 concentrations decreased as distribution system temperatures decreased and increased as distribution system temperatures increased, although the trend is not as clear as it is with THM4. On 4/29/03, 6/11/03 and 8/12/03, the majority of sampling locations exceeded the MCL for HAA5 of 60 µg/L.

As a result of drought conditions at the beginning of the sampling program, bromide concentrations in the raw water were higher than normal. Samples taken on the first two sampling dates, 10/15/02 and 11/18/02 (see Appendix A), contained significant concentrations of tribromoacetic acid (Br<sub>3</sub>AA), dibromochloroacetic acid (Br<sub>2</sub>ClAA), dibromoacetic acid (Br<sub>2</sub>AA) and monobromoacetic acid (BrAA). Subsequent samplings were dominated by trichloroacetic acid (Cl<sub>3</sub>AA) and dichloroacetic acid (Cl<sub>2</sub>AA).

Figure 4.4 presents average THM4 and HAA9 concentrations versus total chlorine residual. Inspection of Figure 4.4 emphasizes the loss in HAAs at location 15 (total chlorine residual of 0.04 mg/L, residence time >120 hours). In contrast, THM4 concentrations do not change at this location relative to concentrations elsewhere in the system. The decrease in HAAs, in conjunction with a loss of total chlorine residual at location 15, occurred to the greatest extent on the warm weather sampling dates.

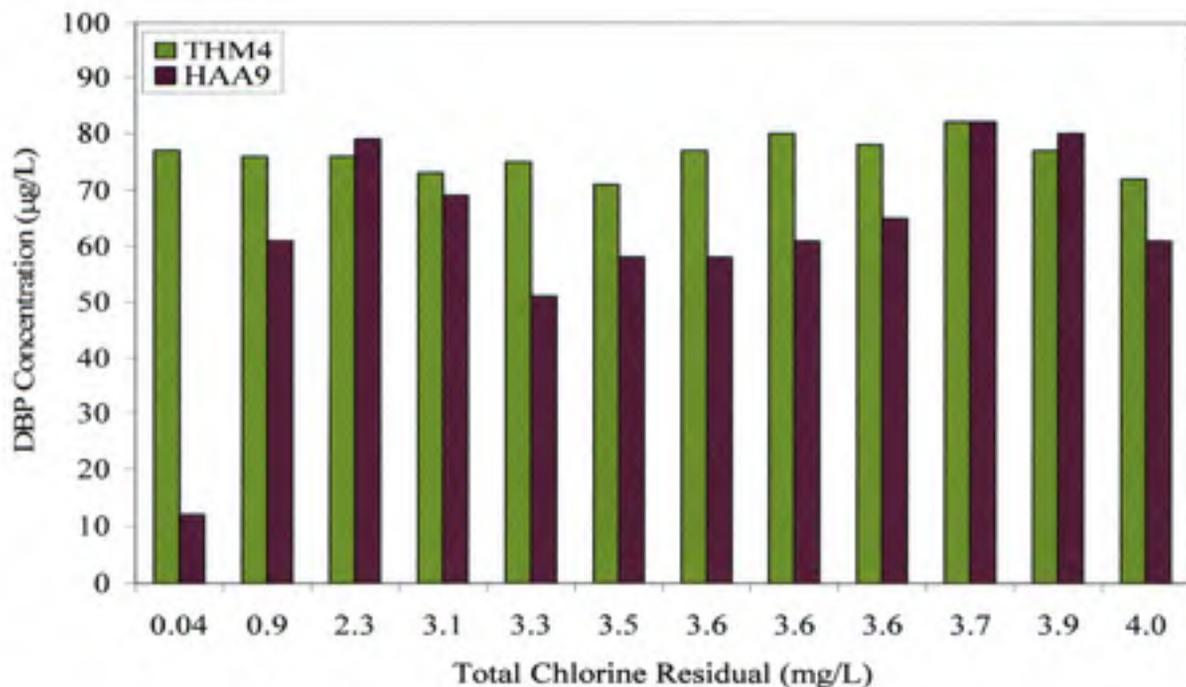


Figure 4.4 THM4 and HAA9 versus total chlorine residual for Utility C for 10/21/03

Table 4.6 presents a statistical summary for THM4 and HAA9 data for all sampling dates. DBP results were calculated as an average across all sampling locations for each sampling date. The range in the coefficient of variation for the THM data is 4–10%, reflecting the ability of monochloramine to control THM formation in the distribution system and keep THM4 concentrations relatively uniform throughout the system. The range in the coefficient of variation for the HAA data is 6–16%, reflecting more variability among HAA9 concentrations throughout the distribution system, despite exclusion of the results from location 15 (residence time >120 hours) which exhibits extensive biodegradation of HAAs. No explanation is available for the greater variability in HAA9 concentrations.

Table 4.6

## Statistical Analysis of THM4 and HAA9 data for Utility C

Date	Average THM4 Concentration ( $\mu\text{g/L}$ )	Standard Deviation	Coefficient of Variation (%)	Average HAA9 Concentration ( $\mu\text{g/L}$ )*	Standard Deviation	Coefficient of Variation (%)
10/15/2002	69	5.8	8	61	8.7	14
11/18/2002	47	4.6	10	73	12	16
1/7/2003	55	2.8	5	53	5.6	11
2/25/2003	55	4.1	7	63	6.5	10
4/29/2003	79	5.5	7	75	5.8	8
6/11/2003	79	5.1	6	65	6.2	9**
8/12/2003	83	6.0	7	85	5.0	6
10/21/2003	76	3.2	4	66	10	16

\* Excludes location 15 where biodegradation caused a loss in HAA concentrations.

\*\*CV does not include one outlier; with the outlier, the CV is 34.

#### 4.1.6 Nitrification

Occurrence of nitrification is characterized by a decrease in ammonia concentration and a corresponding increase in nitrite and nitrate concentrations. Figure 4.5 presents ammonia, nitrite and nitrate concentrations with increasing residence time for 10/21/03. Corresponding figures for the other sampling dates are presented in Appendix A. Evidence of nitrification is seen at sampling location 15 (residence time >120 hours) for all sampling dates and at sampling location 20 (residence time of 8 hours) on 8/12/03 and 10/21/03. Location 15 (residence time >120 hours) is characterized by complete conversion of ammonia to nitrate, whereas location 20 (residence time of 8 hours) is characterized by partial conversion of ammonia to nitrate and appreciable levels of nitrite. Again, it is quite likely that the residence time at the location is much higher than the 8 hours predicted by the hydraulic model. Nitrite concentrations as high as 0.82 mg/L and nitrate concentrations as high as 0.93 mg/L were observed at location 15. High levels of HPCs were seen at locations where evidence of nitrification was observed. Incomplete nitrification, i.e. the oxidation of ammonia to nitrite, can be an issue because nitrite exerts a high chlorine demand (5 mg/L of chlorine as  $\text{Cl}_2$  for 1 mg/L of nitrite as N) (Skadsen 1993).

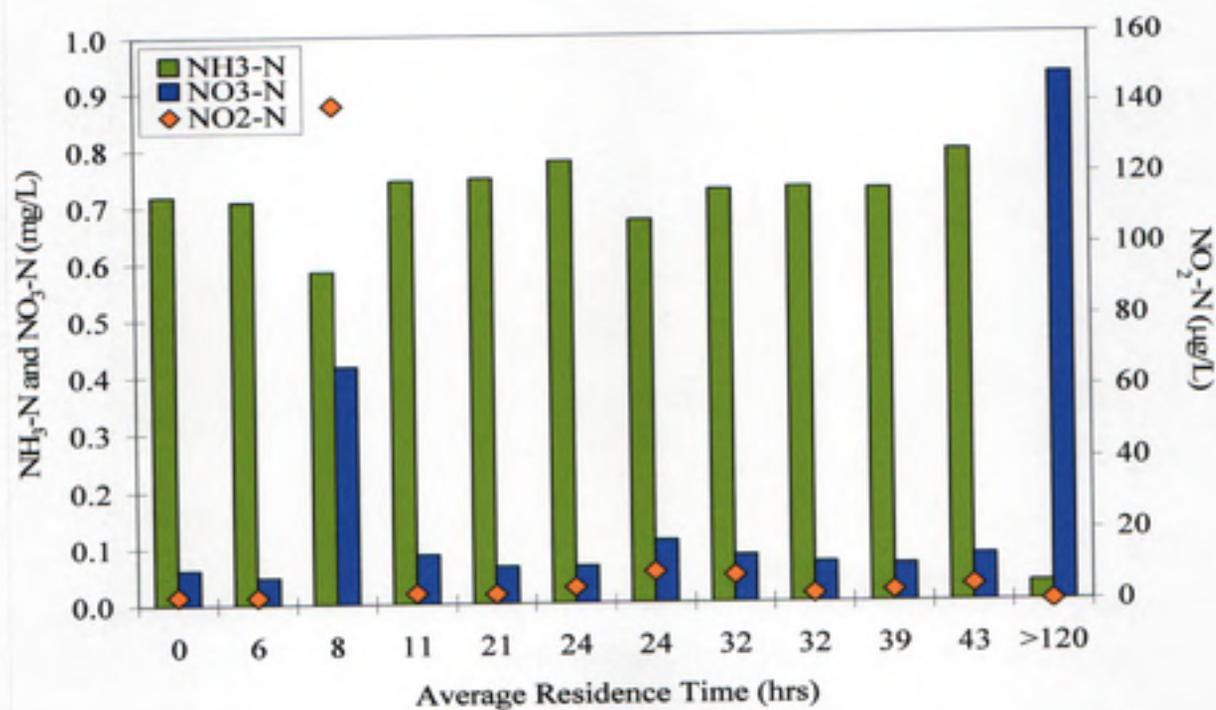


Figure 4.5 Nitrogen species versus average residence time for Utility C for 10/21/03

## 4.2 UTILITY A

Utility A is located in the mid-western portion of the United States. Raw water used for drinking water consists of 60% surface water and 40% ground water. Utility A utilizes free chlorine as a secondary disinfectant and has one booster chlorination station in the distribution system. In addition, there is one storage tank in the distribution system. Utility A was sampled 7 times from October, 2002 through September, 2003.

### 4.2.1 Distribution System Sampling Locations

Utility A utilizes WaterCAD for hydraulic modeling of their distribution system and for estimation of residence times. Thirteen sampling locations were selected to represent a cross-section of residence times found in the distribution system. Residence times were obtained by running the model for 14 days under minimum, average and maximum daily flow conditions. Residence times were determined for five scenarios: minimum daily flow (minimum-flow hour), average daily flow (minimum, average and maximum-hour flow) and maximum daily flow (maximum-flow hour).

Residence times ranged from 0 to 323 hours. In selecting sampling locations, consideration was given to choosing sampling locations that would incorporate the distribution system storage tank and the booster chlorination station. In addition to residence time, pipe material and pipe diameter were included in the criteria for selecting sampling locations. Three different pipe materials are represented: cast iron, ductile iron and transite. Pipe diameters ranged from 8 to 16 inches. Table 4.7 presents residence times, pipe material and pipe diameter data for each sampling location.

Table 4.7  
Sample site characteristics for Utility A

Sample ID	Pipe Diameter (in.)	Pipe Material	Residence Time (hrs)			Comments
			Min	Avg	Max	
EP001	16	CI	0	0	0	
MR001**	16	DI	6	95	8	
RD002	10	CI	6	8	7	
RD004	8	TR	19	18	14	
RD005	16	DI	18	8	11	
RD007	8	CI	5	6	5	
RD013	8	TR	5	5	5	
RD018	16	CI	3	4	3	
RD020	12	DI	197	201	198	Rechlorination point
RD025	8	DI	313	323	317	
RD027	12	DI	89	100	95	
RD028	12	DI	197	201	198	
RD029*	16	DI	6	95	8	

- \* Located before a storage reservoir
- \*\* Located after a storage reservoir
- Located before a rechlorination booster station
- Located after a rechlorination booster station
- CI Cast Iron
- DI Ductile Iron
- TR Transite

#### 4.2.2 Distribution System Sampling Results

Tables 4.8 through 4.11 present temperature, pH, chlorine residual, organic carbon, microbiological, THM4 and HAA9 data for Utility A for 9/09/03. Data for the other sampling dates are presented in Appendix B.

Samples for AOC were taken only at the point of entry to the distribution system. TOC and UV254 were measured at all sampling locations for the first two sampling dates; for subsequent samplings, TOC and UV254 were measured only at the point of entry. AOC concentrations in the treated water ranged from 203 to 740  $\mu\text{g/L}$  for all sampling dates. TOC concentrations at the point of entry ranged from 1.19 to 2.85  $\text{mg/L}$ . UV254 values at the point of entry ranged from 0.026 to 0.045  $\text{cm}^{-1}$ .

Temperature and pH were measured at all sampling locations for all sampling dates. pH values at the point of entry ranged from 8.7 to 9.5 and from 8.0 to 9.4 within the distribution system. Distribution system temperatures ranged from 4.0 to 25.0°C.

Table 4.8  
pH, temperature and chlorine data for Utility A for 9/23/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
EP001	17	9.1	3.3	3.7
MR001	16	9.3	1.6	1.7
RD002	16	9.4	2.6	2.6
RD004	18	9.3	1.5	1.8
RD005	16	9.4	2.4	2.4
RD007	18	9.2	2.2	3.0
RD013	18	9.3	2.6	2.8
RD018	17	9.4	2.9	2.9
RD020	17	9.3	0.9	1.0
RD025	18	9.3	0.3	0.4
RD027	25	9.3	0.3	0.5
RD028	17	9.3	0.8	1.1
RD029	18	9.2	1.4	1.8

Table 4.9

Organic carbon and microbiological data for Utility A for 9/23/03

Sample ID	AOC (mg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
EP001	203	2.85	0.034	NA*
MR001				<100
RD002				1.9E+02
RD004				1.2E+03
RD005				6.5E+02
RD007				4.3E+02
RD013				1.4E+03
RD018				2.6E+02
RD020				1.2E+03
RD025				2.1E+03
RD027				9.2E+02
RD028				4.0E+02
RD029				1.6E+02

\* NA Not Available

Table 4.10

Trihalomethane (THM) data (in µg/L) for Utility A for 9/23/03

Sample ID	CHCl <sub>3</sub> *	BrCl <sub>2</sub> CH	Br <sub>2</sub> ClCH	CHBr <sub>3</sub>	THM4
EP001	39	11	5	<1	55
MR001	62	21	11	3	97
RD002	120	27	11	<1	158
RD004	107	28	12	<1	146
RD005	65	22	12	<1	99
RD007	58	19	11	1	89
RD013	59	17	10	1	88
RD018	54	15	10	2	81
RD020	150	29	9	<1	188
RD025	165	33	11	<1	209
RD027	143	29	10	<1	182
RD028	143	28	9	<1	180
RD029	118	28	11	<1	157

\*Matrix spike did not meet QA/QC requirements

Table 4.11

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility A for 9/23/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
EP001	<2	<2	13	3	<2	4	4	2	<2	25
MR001	4	<2	27	7	2	7	5	2	<2	55
RD002	2	<2	17	5	2	4	5	2	<2	38
RD004	3	<2	23	6	2	6	5	2	<2	48
RD005	3	<2	17	6	2	4	5	3	<2	40
RD007	3	<2	16	5	2	4	4	2	<2	37
RD013	3	<2	16	5	2	5	4	2	<2	38
RD018	3	<2	18	5	2	4	4	3	<2	40
RD020	<2	<2	9	2	<2	9	4	2	<2	27
RD025	<2	<2	12	3	<2	9	4	2	<2	31
RD027	<2	<2	8	2	<2	9	4	2	<2	27
RD028	<2	<2	10	3	<2	9	4	2	<2	29
RD029	5	<2	26	7	2	7	5	2	<2	55

### 4.2.3 Chlorine Residual

The average total chlorine residual measured at the point of entry to the distribution system for all sampling dates was 3.2 mg/L, with a range of 2.6–3.7 mg/L. Essentially all of the residual was free chlorine. Figure 4.6 illustrates the relationship between residence time and free chlorine residual throughout Utility A's distribution system for samples taken on 9/23/03. Corresponding figures for the other sampling dates are presented in Appendix B. A reduction in chlorine residual can be observed as residence time increases for most sampling dates. This observation is consistent with the literature and the chemistry of chlorine, as chlorine has a greater tendency to participate in redox reactions in the bulk phase and at the pipe walls, especially in reactions involving iron pipes (Vasconcelos et al. 1997; Kiene, Lu and Levi 1998; Baribeau et al. 2001). The magnitude of the decrease in chlorine residual varies throughout the distribution system. At several locations, the chlorine residual decreases significantly. The greatest decrease was observed during the warmer months, an observation that is also consistent with the literature (Kiene, Lu and Levi 1998; Baribeau et al. 2001). The greatest loss in chlorine residual was consistently observed at location RD025 (residence time of 323 hours). A decrease in chlorine residual was also observed at location RD027 (residence time of 100 hours), although not to the same extent as that typically seen at RD025. For four out of the seven sampling dates,

location RD025 (residence time of 323 hours) had less than 0.5 mg/L of residual chlorine. Despite the presence of a chlorine booster station between locations RD028 and RD020 (residence times of 201 hours), chlorine residuals at RD020, immediately after the chlorine booster station, did not increase appreciably.

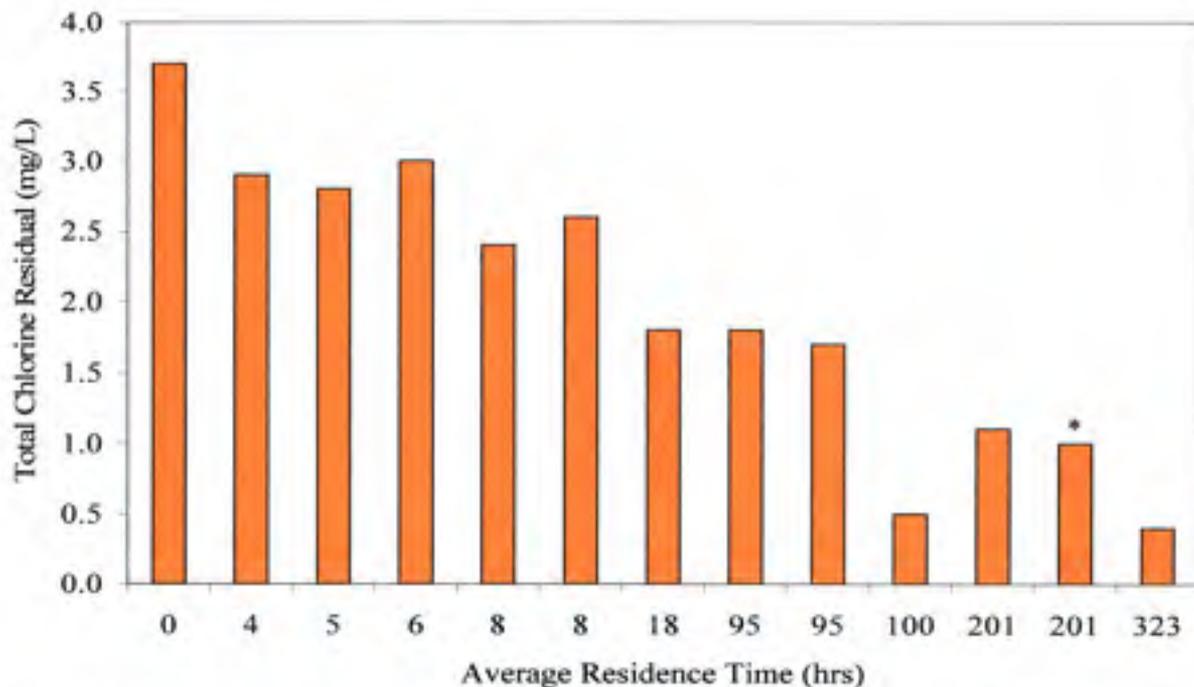


Figure 4.6 Total chlorine residual versus average residence time for Utility A for 9/23/03 (\* indicates a location after rechlorination.)

#### 4.2.4 Heterotrophic Plate Counts

Figure 4.7 presents changes in HPCs and chlorine residual as residence time increases. Corresponding figures for the other sampling dates are presented in Appendix B. HPCs were measured at the point of entry to the system for only four of the seven sampling dates. HPCs increased as total chlorine residual decreased, a trend observed for all sampling dates. This observation is consistent with results obtained by Prevost and Rompre et al (1998) and Zhang and DiGiano (2002). The majority of sampling locations consistently had HPC greater than  $10^2$  CFU/mL for most sampling dates, despite the presence of a chlorine residual of 1 mg/L or greater. In addition, an increase in HPCs was observed as residence time increased, which is consistent with the findings of Zhang and DiGiano (2002). Sampling locations with residence

times greater than or equal to 95 hours had the highest HPCs for all sampling dates. Despite rechlorination at location RD020 (residence time of 201 hours), HPCs in excess of  $10^2$  CFU/mL were consistently (five out of seven sampling dates) measured at locations RD020 and RD025 (residence time of 201 and 323 hours, respectively). The June sampling had the highest overall HPCs of all the sampling dates.

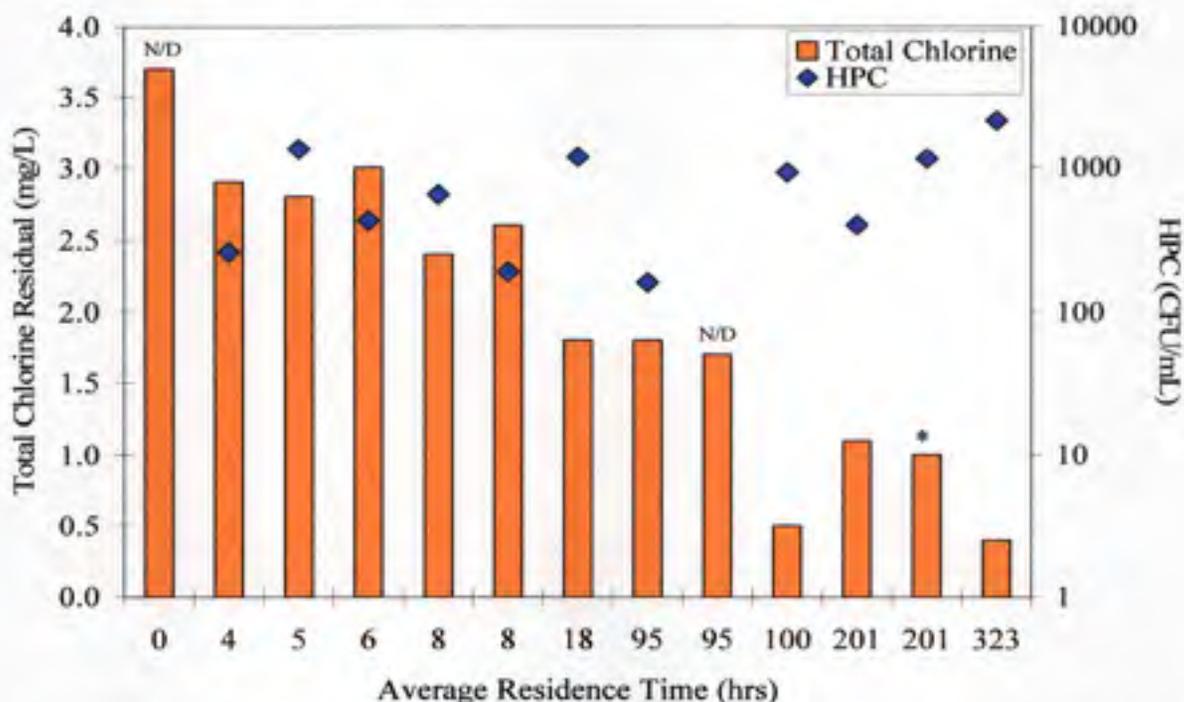


Figure 4.7 Total chlorine residual and HPC versus average residence time for Utility A for 9/23/03. (\* indicates a location after rechlorination.)

#### 4.2.5 Disinfection By-Product Formation

Figure 4.8 presents average THM4 and HAA9 concentrations and chlorine residuals as residence time increases for sampling conducted on 9/23/03. Corresponding figures for the other sampling dates are presented in Appendix B. THM4 concentrations increase as residence time increases and chlorine residual decreases, a trend observed for all sampling dates. This pattern is consistent with the literature and theoretical expectations (Bellar, Lichtenberg and Kroner 1974; Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Krasner et al. 1996; Baribeau et al. 2001; Singer 2001; Dickenson, Work and Summers 2002; Pope, Speitel et al. 2002). THM4 concentrations at the point of entry were always the lowest values, while THM4 concentrations

at sampling location RD025 (residence time of 323 hours) were always the highest values. THM4 concentrations were lowest in the colder months and highest in the warmer months, with the highest concentrations measured during the August sampling. Again, this is consistent with the literature (Singer 2001; Dickenson, Work and Summers 2002; Rodriguez et al. 2002).

Chloroform ( $\text{CHCl}_3$ ) and bromodichloromethane ( $\text{CHBrCl}_2$ ) comprised 80–97% of the THM4 concentrations for all sampling dates, with  $\text{CHCl}_3$  consisting of at least 50% of the THM4 concentration. The impact of rechlorination before RD020 (residence time of 201 hours) on THM levels is difficult to discern. THM4 concentrations at sampling location RD025 (residence time of 323 hours) exceeded the MCL for THM4 of 80  $\mu\text{g/L}$  for all sampling dates; THM4 concentrations above 160  $\mu\text{g/L}$  were measured for five out of seven sampling dates. On three out of the seven sampling dates, only the point of entry THM4 concentration was below the MCL.

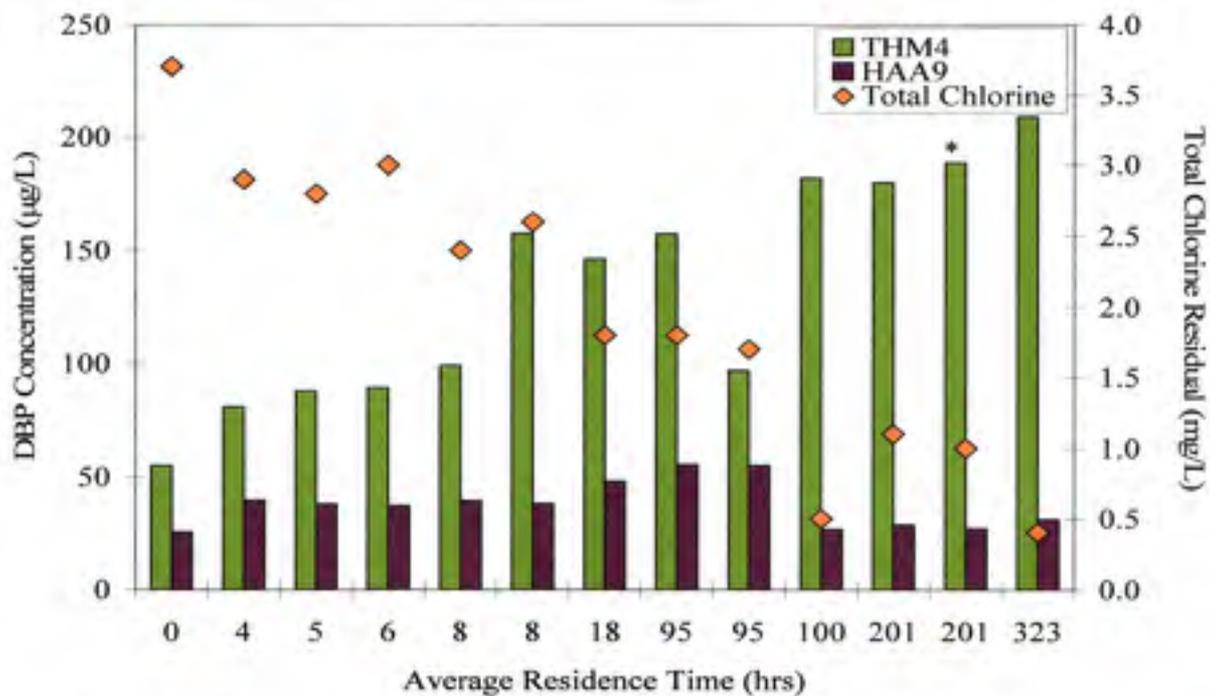


Figure 4.8 THM4, HAA9 concentrations and total chlorine residual versus average residence time for Utility A for 9/23/03. (\* indicates a location after rechlorination.)

Figure 4.8 also presents average HAA9 concentrations as residence time increases for sampling conducted on 9/23/03. HAA9 concentrations increased as residence time increased and chlorine residual decreased, except at sampling locations with residence times above 95 hours, where a decrease in HAA9 concentrations was seen. This pattern was observed for the majority of sampling dates, but was most noticeable during the late summer and fall sampling dates and less so during the colder months.

The lowest HAA9 concentrations were not always observed at the point of entry to the distribution system. During four of the seven sampling dates, the lowest HAA9 concentrations occurred at sampling locations with residence times of 100 hours or greater. In particular, sampling locations RD027, RD028 and RD025 (residence times of 100, 201 and 323 hours, respectively) exhibited signs of HAA9 biodegradation despite the presence of a free chlorine residual in excess of 0.5 to 1 mg/L at some of these locations (See Figure 4.9). HAA9 biodegradation has been observed at high residence time locations in a number of distribution systems (Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995; Williams, Williams and Gordon 1996; LeBel, Benoit and Williams 1997; Chen and Wiesel 1998), but typically at locations with low disinfectant residuals and high HPCs (Williams, Williams and Rindfleisch 1994; Williams, Williams and Gordon 1995).

For most of the sampling dates the dominant HAA9 species were the dihaloacetic acids, followed by the trihaloacetic acids. Loss of the mono- and di-haloacetic acids was more pronounced than losses in the trihaloacetic acids, which is consistent with the literature on HAA biodegradation (van der Ploeg, van Hall and Janssen 1991; Williams, Williams and Gordon 1995). An average decrease of 62% in HAA9 concentrations was observed (from the maximum value to the lowest value), with a maximum decrease of 93%. HAA9 concentrations did not reach 0 µg/L at any time during the sampling period, although concentrations of less than 10 µg/L were observed. Total HAA9 concentrations were lowest in the colder months and highest in the warmer months. HAA9 concentrations never exceeded 60 µg/L. This may be a result of the relatively high pH (often > 9) of the finished water. HAA formation tends to decrease with increasing pH (Stevens, Moore and Miltner 1989; Symons et al. 1996; Singer 1999; Singer 2001).

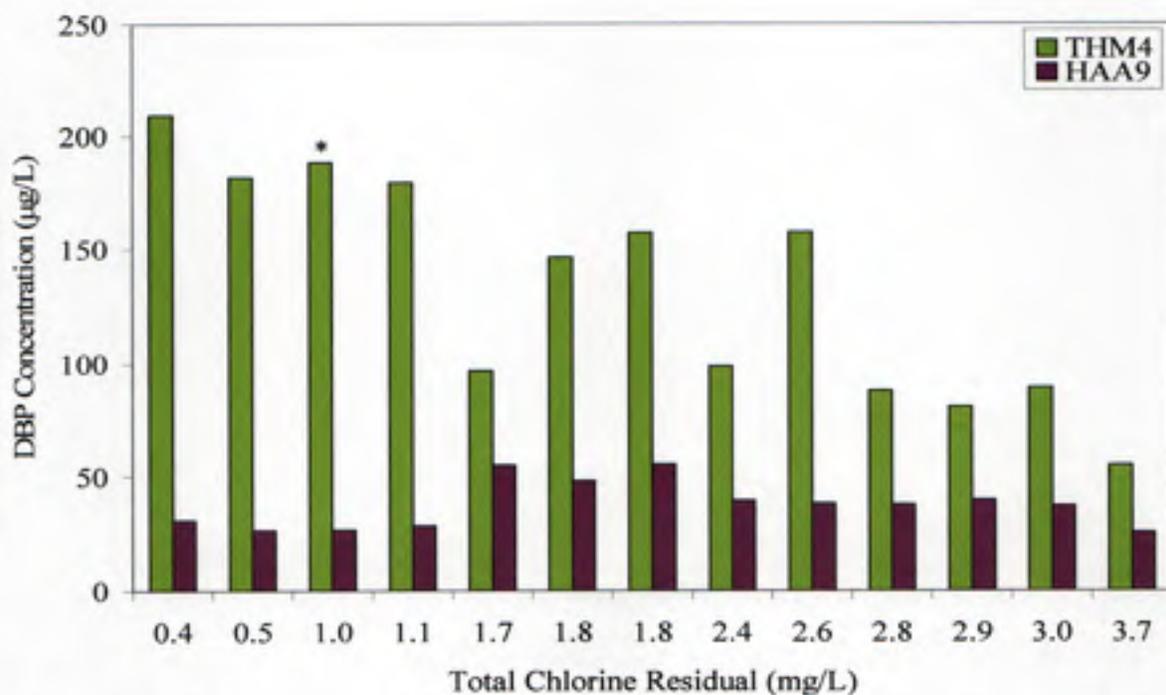


Figure 4.9 THM4 and HAA9 concentration versus total chlorine residual for Utility A for 9/23/03. (\* indicates a location after rechlorination.)

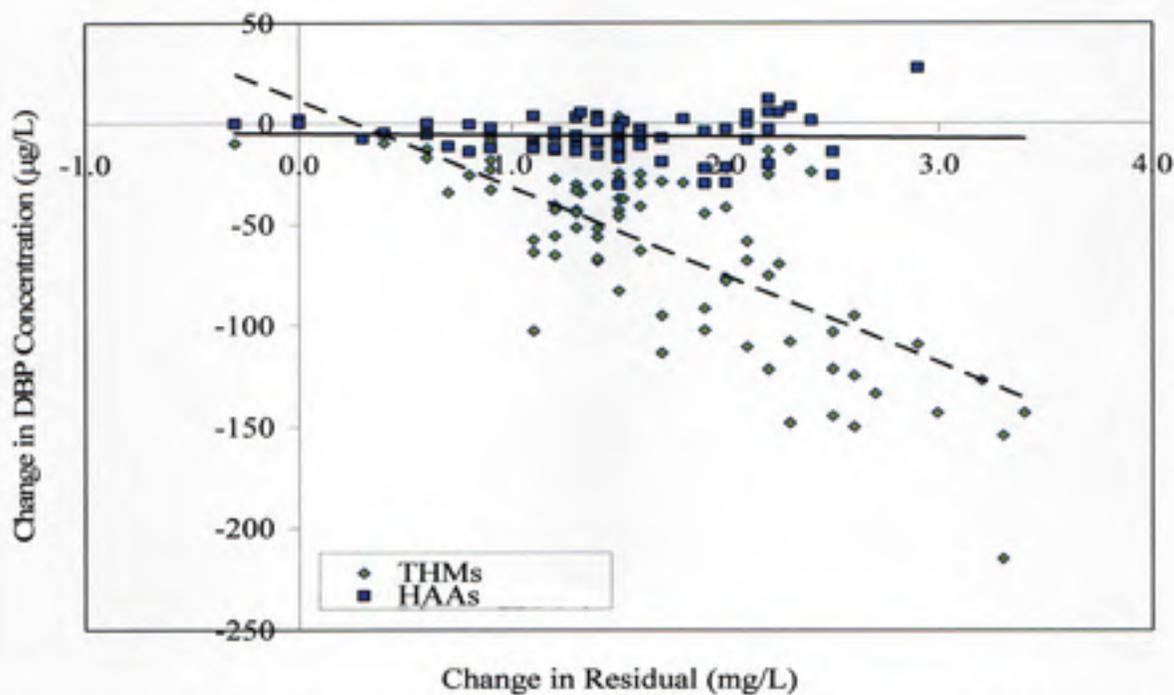


Figure 4.10 Changes in THM4 and HAA9 concentration versus changes in total chlorine residual in the distribution system for Utility A for all sampling dates.

Figure 4.10 presents the change in DBP concentrations and the change in chlorine residual as compared to measurements taken at the point of entry for all sampling dates. An approximately linear increase in THM4 concentration can be seen as a decrease in chlorine residual occurs. In contrast, no increase in HAA9 concentration with a decrease in chlorine is seen.

## **4.3 UTILITY B**

Utility B is located in the southern portion of the United States. Source water used for drinking water is 100% surface water. Utility B utilizes free chlorine both as a primary and secondary disinfectant, with no booster chlorination in the distribution system. Utility B was sampled 8 times from October, 2002 through October, 2003.

### **4.3.1 Distribution System Modeling**

Utility B utilizes the HAESTAD (Waterbury, CT) hydraulic model to model their distribution system and estimate water age. Average residence times were obtained by running the model at average flow and demand conditions. Fourteen sampling locations were selected to represent a cross-section of residence times found in the distribution system. Average residence times ranged from 0 to 47 hours. In addition to residence time, pipe material and pipe diameter were included in the criteria for selecting sampling locations. Ten sampling locations were located along a 30-inch diameter ductile iron transmission main and four sampling locations were located on 4-inch diameter PVC pipes. Table 4.12 presents water age results obtained from the model, as well as pipe material and pipe diameter data for each sampling location.

Table 4.12

## Sample site characteristics for Utility B

Sample ID	Pipe Diameter (in.)	Pipe Material	Average Residence Time (hrs)
POE	30	DI	0
308	30	DI	5
883	30	DI	11
975	30	DI	14
979	30	DI	19
208	30	DI	24
232	30	DI	29
100	30	DI	34
116	30	DI	39
251	30	DI	44
227	30	DI	47
X-3	4	PVC	9
R-1	4	PVC	27
D-6	4	PVC	34
X-11	4	PVC	12

DI Ductile Iron

PVC Polyvinyl chloride

#### 4.3.2 Distribution System Sampling Results

Tables 4.13 through 4.16 present free and total chlorine, pH, temperature, organic carbon, microbiological, THM4 and HAA9 data for Utility B for 4/29/03. Data for the other sampling dates are presented in Appendix C.

At the point of entry to the distribution system, samples were taken to measure AOC. TOC and UV254 were measured at all sampling locations in the distribution system. AOC concentrations in the treated water varied considerably, and ranged from 71 to 855  $\mu\text{g/L}$  over all sampling dates. No seasonal pattern was apparent. Point of entry TOC concentrations ranged from 1.69 to 1.98  $\text{mg/L}$  and fluctuated between 1.37 and 2.59  $\text{mg/L}$  within the distribution system. UV254 values ranged from 0.020 to 0.029  $\text{cm}^{-1}$  at the point of entry and from 0.018 to 0.044  $\text{cm}^{-1}$  in the distribution system.

Temperature and pH were measured at all sampling locations for all sampling dates. pH values at the point of entry ranged from 8.80 to 9.05, and from 8.33 to 9.15 within the distribution system. pH values were on the high side because of the corrosion control strategy

employed by the utility. Distribution system temperatures ranged from 8.0 to 27.0°C. Although Utility B does have small amounts of bromide in their source water, bromide measurements were not made.

Table 4.13  
pH, temperature and chlorine data for Utility B for 4/29/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
WTP	22	8.9	1.8	2.0
308	24	8.8	1.8	1.8
883	23	8.8	1.8	1.8
975	24	8.8	1.8	1.9
979	N/S	N/S	N/S	N/S
208	21	8.8	1.7	1.8
232	22	8.8	1.7	1.8
100	21	8.9	1.6	1.7
116	21	8.9	1.5	1.6
251	22	8.8	1.7	1.7
227	21	8.9	1.5	1.6
X-3	22	8.8	1.8	1.9
R-1	22	8.8	1.8	1.9
D-6	N/S	N/S	N/S	N/S
X-11	22	8.8	1.8	1.9

N/S = Not Sampled

Table 4.14

Organic carbon and microbiological data for Utility B for 4/29/03

Sample ID	AOC ( $\mu\text{g/L}$ )	TOC ( $\text{mg/L}$ )	UV254 ( $\text{cm}^{-1}$ )	HPC (CFU/mL)
WTP	139	1.54	0.024	<10
308		1.50	0.024	1.5E+01
883		1.51	0.025	1.0E+02
975		1.64	0.025	1.5E+01
979		N/S	N/S	N/S
208		1.51	0.024	2.0E+01
232		1.49	0.025	2.9E+02
100		1.79	0.024	7.4E+02
116		2.63	0.029	7.4E+02
251		1.53	0.023	6.8E+02
227		1.85	0.025	5.6E+02
X-3		1.54	0.025	2.0E+02
R-1		1.55	0.026	1.5E+02
D-6		N/S	N/S	N/S
X-11		1.76	0.026	1.9E+02

N/S = Not Sampled

Table 4.15

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility B for 4/29/03

Sample ID	$\text{CHCl}_3$	$\text{BrCl}_2\text{CH}$	$\text{Br}_2\text{ClCH}$	$\text{CHBr}_3$	THM4
WTP	32	7	2	<1	41
308	39	10	2	<1	51
883	42	11	2	<1	55
975	39	10	2	<1	51
979	N/S	N/S	N/S	N/S	N/S
208	35	10	2	<1	47
232	46	11	3	<1	60
100	45	10	2	<1	57
116	50	10	2	<1	62
251	40	9	2	<1	51
227	49	9	2	<1	60
X-3	33	8	2	<1	43
R-1	32	7	2	<1	41
D-6	N/S	N/S	N/S	N/S	N/S
X-11	33	7	2	<1	42

N/S = Not Sampled

Table 4.16

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility B for 4/29/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
WTP	<2	2	16	3	1	6	3	<1	<1	31
308	<2	2	18	4	2	7	3	<1	<1	36
883	<2	2	17	3	1	6	3	<1	<1	32
975	<2	2	15	3	1	6	3	<1	<1	30
979	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
208	<2	2	15	3	2	6	3	<1	<1	31
232	<2	2	20	4	2	7	3	<1	<1	38
100	<2	2	23	4	2	9	3	<1	<1	43
116	3	<1	25	3	1	8	3	<1	<1	43
251	<2	2	22	4	<1	9	3	<1	<1	40
227	<2	1	25	4	1	9	3	<1	<1	43
X-3	<2	2	19	4	2	7	3	<1	<1	37
R-1	<2	2	17	3	<1	7	3	<1	<1	32
D-6	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
X-11	<2	2	20	4	1	7	3	<1	<1	37

N/S = Not Sampled

### 4.3.3 Chlorine Residual

The average total chlorine residual measured at the point of entry to the system for all sampling dates was 2.02 mg/L, with a range of 1.10–2.11 mg/L in the distribution system. The majority of the residual was free chlorine. Chlorine residuals never fell below 1 mg/L at any of the selected locations on any of the sampling dates. Figure 4.11 illustrates the relationship between residence time and total chlorine residual for samples taken on 4/29/03. Corresponding figures for the other sampling dates are presented in Appendix C. A slight decrease in total chlorine residual is observed as residence time increases; this trend was seen for all sampling dates. This pattern is similar to that seen for Utility A, although the loss in chlorine residual is much smaller. The average loss in total chlorine residual throughout the distribution system for all sampling dates was 0.69 mg/L, with a range of 0.31–1.00 mg/L.

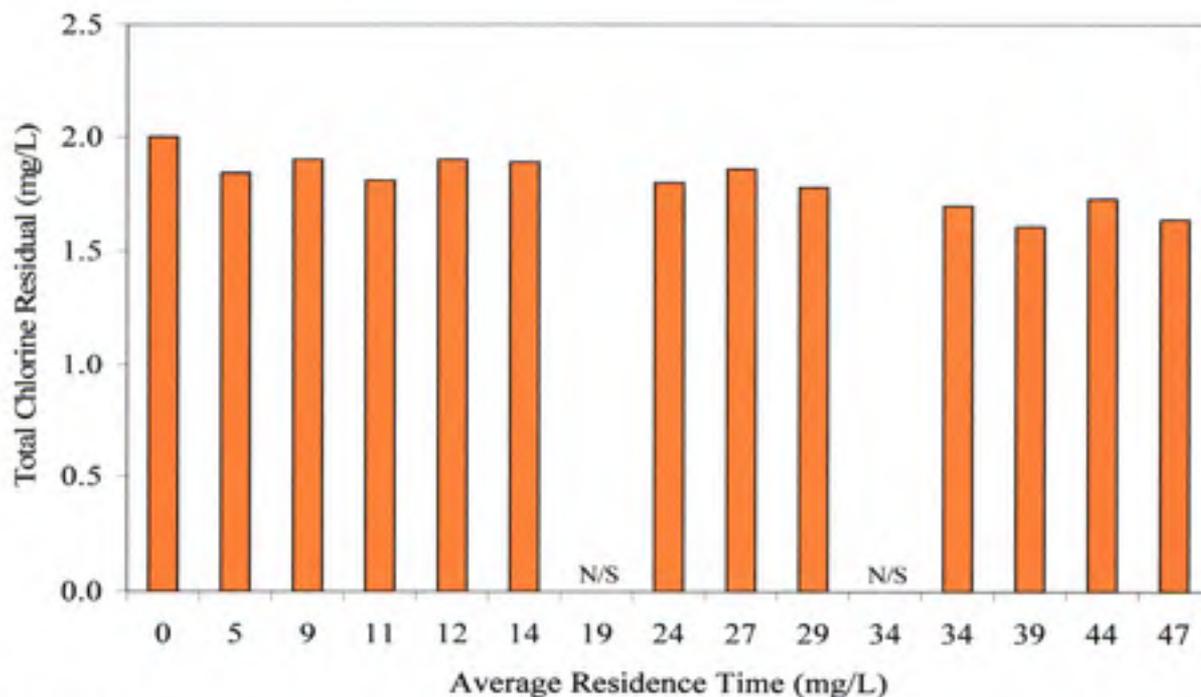


Figure 4.11 Total chlorine residual versus average residence time for Utility B for 4/29/03. (N/S = Not Sampled)

#### 4.3.4 Heterotrophic Plate Counts

Figure 4.12 presents changes in HPCs and total chlorine residual as residence time increases for sampling on 4/29/03. Corresponding figures for the other sampling dates are presented in Appendix C. For all sampling dates, the majority of samples had HPCs less than 1000 CFU/mL. For all sampling dates, seven samples had HPCs between 1000 and 10,000 CFU/mL and one sample had an HPC greater than 10,000 CFU/mL. There was no apparent pattern between the magnitude of the HPCs and total chlorine residual or residence time, although higher HPCs were observed during the warmer months. Elevated HPCs were seen even at sampling locations with total chlorine residuals greater than 1.5 mg/L (see Figure 4.12).

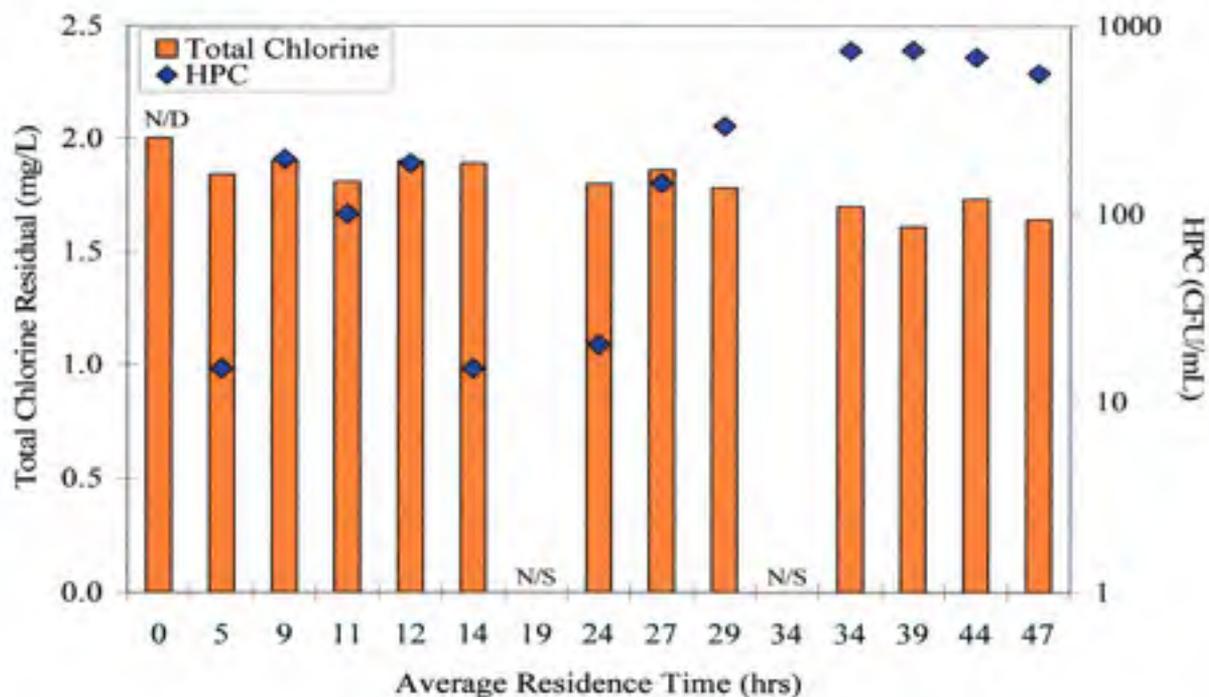


Figure 4.12 Total chlorine residual and HPC versus average residence time for Utility B for 4/29/03. (N/S = Not Sampled)

#### 4.3.5 Disinfection By-Product Formation

Figures 4.13 and 4.14 present THM4 and HAA9 data with increasing residence time and increasing total residual chlorine concentration, respectively, for Utility B for sampling date 4/29/03. As expected, THM4 concentrations tend to increase as residence time increased and as chlorine residual decreased, a trend found for all sampling dates. There is some variation in the increase in THM4 concentrations with residence time but, overall, THM4 concentrations increased from the point of entry to the sampling locations with the highest residence times. THM4 concentrations were higher than HAA9 concentration, most likely due to the high pH of the finished water. THM4 and HAA9 concentrations appear to be correlated more with total chlorine residual than with residence time. As total chlorine residual decreased, THM4 and HAA9 concentrations increased; this pattern is seen for the majority of sampling dates. No evidence of biodegradation of HAAs was observed, most likely as a result of the high chlorine residuals at all sampling locations. The associations between residence time, disinfectant residual, and DBP formation have been noted by other researchers (Bellar, Lichtenberg and

Kroner 1974; Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Krasner et al. 1996; Baribeau et al. 2001; Singer 2001; Dickenson, Work and Summers 2002; Pope et al. 2002).

THM4 and HAA9 concentrations decreased as distribution system temperatures decreased and increased as distribution system temperatures increased; peak concentrations for both classes of DBPs occurred in June. This pattern is consistent with the literature and with theory (Krasner et al. 1996). THM4 concentrations exceeded the 80  $\mu\text{g/L}$  MCL at various sampling locations on five out of the eight sampling dates. HAA9 variability between sampling locations seemed to be correlated with THM4 variability between sampling locations, except for the November sampling during which HAA9 concentrations exceeded THM4 concentrations at several sampling locations. HAA5 concentrations exceeded the 60  $\mu\text{g/L}$  MCL at several sampling locations on three out of the eight sampling dates.

A figure similar to Figure 4.10 for Utility A was constructed for Utility B to quantitatively compare the additional production of THMs and HAAs in the distribution system with the corresponding decrease in chlorine residual, but no relationship was evident. This is likely due to the stability of the chlorine residual in Utility B system, i.e., the chlorine residual in the distribution system decreased by less than 1.0 mg/L from the point of entry value for each of the sampling periods.

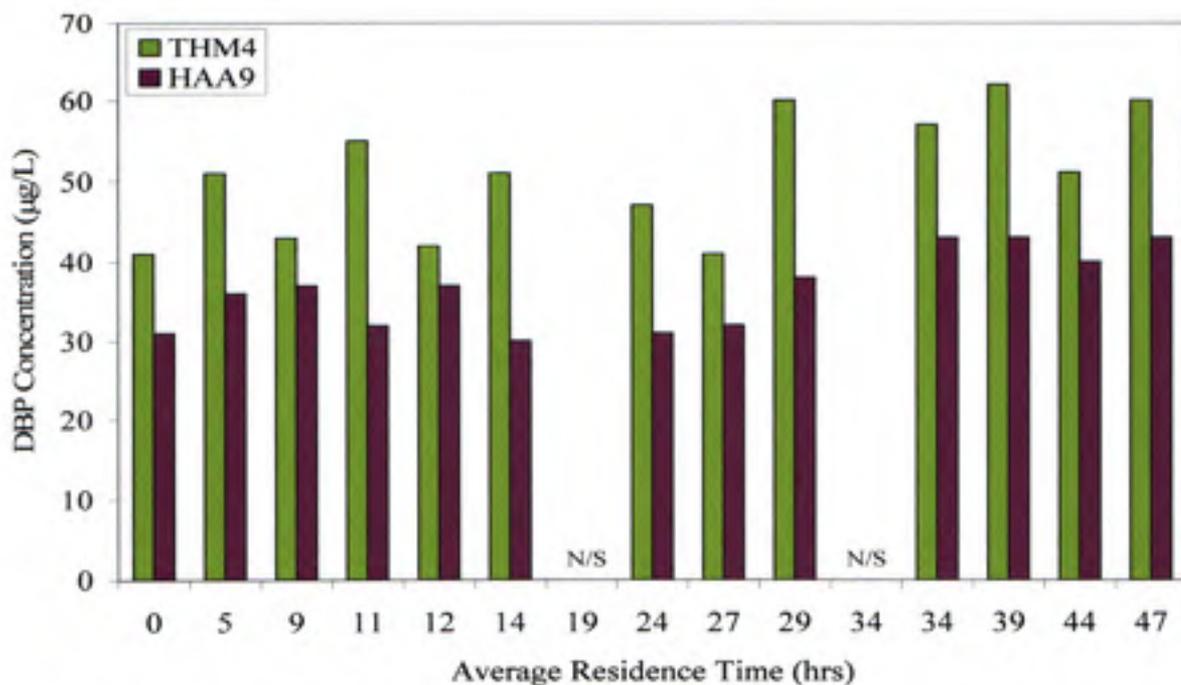


Figure 4.13 THM4 and HAA9 concentration versus average residence time for Utility B for 4/29/03. (N/S = Not Sampled)

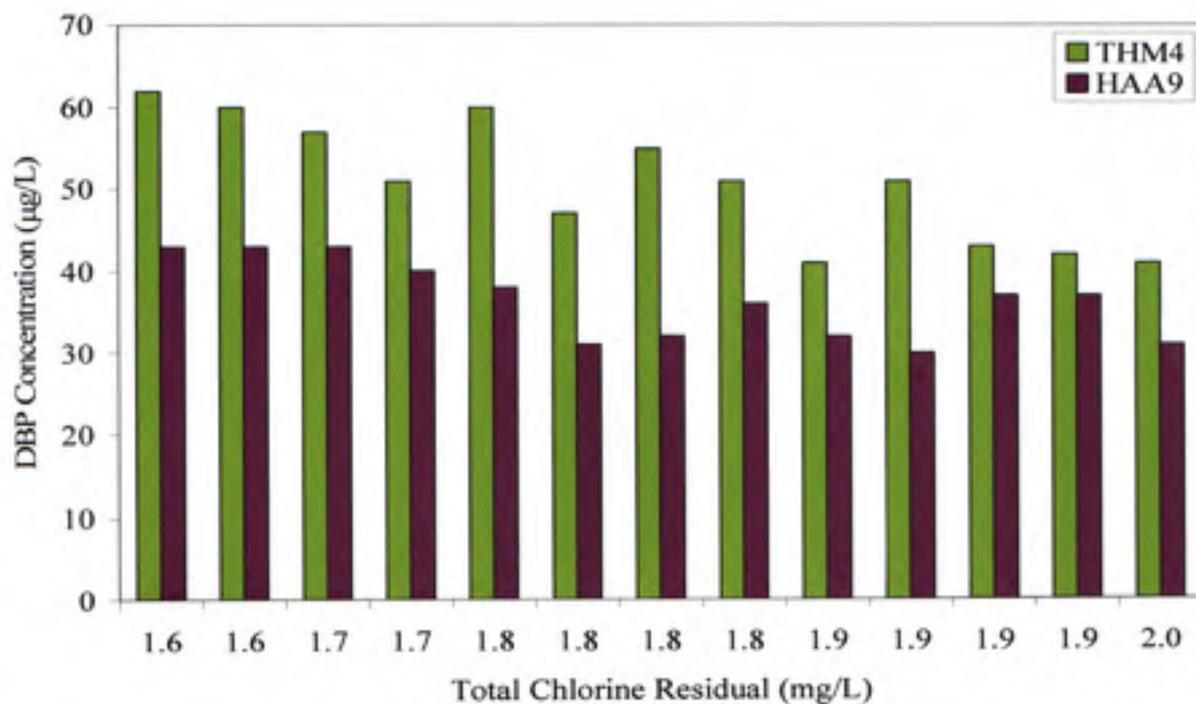


Figure 4.14 THM4 and HAA9 concentration versus total chlorine residual for Utility B for 4/29/03

## 4.4 UTILITY D

Utility D is located in the western portion of the United States. Water is taken from a surface water source and tends to have relatively high bromide concentrations. Utility D utilizes chloramines as a secondary disinfectant, but does not routinely switch to free chlorine. One section of Utility D's distribution system was chosen for this study. The section of Utility D's distribution system that was chosen for sampling contained no storage reservoirs or booster chlorination stations. Utility D was sampled six times from November, 2002 through September, 2003.

### 4.4.1 Distribution System Modeling

Utility D employs H2ONET as a hydraulic model. Residence times were obtained by running the model for 72 hours at average flow and demand. Sixteen sampling locations were chosen to represent a cross-section of residence times found in the distribution system. Three different pipe materials were chosen as representative of the distribution system: cast iron, PVC and asbestos cement.

During the course of the study, Utility D had to supplement their traditional point of entry to the distribution system with a second point of entry. Both points of entry use the same treated water. As a result of adding the second point of entry, flow and demand patterns changed for the different sampling dates. Consequently, the hydraulic model was rerun producing four different residence time scenarios, each dependent on the relative distribution of flows into the portion of the distribution system studied. Tables 4.17 illustrates model results obtained for two different flow scenarios, on 4/8/2003 and 1/07/2003. Results for the other scenarios on the other sampling dates are located in Appendix D. A major impact of the changing flow patterns is the change in residence times for the different sampling locations. The average residence times calculated for each scenario were used in the subsequent analysis of all sampling data. A weighted water age was calculated by the model based on the proportion of water that came from each point of entry. Table 4.18 presents the average residence times for each sampling location under each of the four hydraulic scenarios. Changes in residence time are significant for some locations, e.g. from 2 to 37 hours at Site 10, and minor at other locations, e.g. 2 to 5 hours at Site 2.

As a result of the changes in residence times at each location for the different sampling dates, it is difficult to generalize results across sampling dates. The results presented in subsequent sections were selected to illustrate how changes in the hydraulic operation of the distribution system and changing residence times affected residual chlorine profiles, DBP formation and decay, and nitrification. The results for 4/8/2003 and 1/07/2003 were selected for this purpose.

Table 4.17  
Sample site characteristics for Utility D for 4/08/03 and 1/07/03

Sample ID	Address	Pipe Diameter (in.)	Pipe Material	Avg Residence Time (hrs)	
				4/8/2003	1/7/2003
Site 1	WB-2A	12	CI	0	0
Site 2	4732 Manhattan	12	AC	3	2
Site 3	16102 Inglewood	8	CI	3	2
Site 4	16310 Inglewood	8	CI	4	3
Site 5	16612 Inglewood	8	CI	4	6
Site 6	7102 Inglewood	6	CI	6	11
Site 7	4748 173rd	4	CI	13	18
Site 8	4700 172nd			8	
Site 9	17305 Condon			14	
Site 10	16817 Praire	6	AC	2	37
Site 11	4140 162nd	4	CI	2	11
Site 12	WB-11			0	
Site 13	4641 Artesia				
Site 14	4749 Artesia Blvd	4	CI		50
Site 15	4416 170th	8	CI		15
Site 16	16514 Grevillea	8	PVC		8

CI Cast Iron

PVC Poly vinyl chloride

AC Asbestos Cement

Table 4.18

Average residence time for all hydraulic scenarios for Utility D

Sample ID	Address	Average Residence Time (hrs) by Date					
		11/8/2002	1/7/2003	4/8/2003	6/10/2003	7/22/2003	9/23/2003
Site 1	WB-2A (Point of Entry)	0	0	0		0	0
Site 2	4732 Manhattan	2	2	3	5	2	2
Site 3	16102 Inglewood	2	2	3	6	3	3
Site 4	16310 Inglewood	3	3	4	8	3	3
Site 5	16612 Inglewood	6	6	4	8	4	4
Site 6	7102 Inglewood	11	11	6	13	4	7
Site 7	4748 173rd	18	18	13	15	11	11
Site 8	4700 172nd			8	15	9	9
Site 9	17305 Condon			14	21	13	13
Site 10	16817 Praire	37	37	2	4	3	3
Site 11	4140 162nd	11	11	2			
Site 12	WB-11 (Point of Entry)			0	0	0	0
Site 13	4641 Artesia				20	10	10
Site 14	4749 Artesia Blvd	50	50				
Site 15	4416 170th	15	15				
Site 16	16514 Grevillea	8	8				

#### 4.4.2 Distribution System Sampling Results

Tables 4.19 through 4.26 present sampling results obtained for chlorine residual, temperature, pH, organic carbon, HPCs, nitrogen, bromide, and THM4 and HAA9 for Utility D for sampling dates 4/08/03 and 1/07/03. Results for the other sampling dates are presented in Appendix D.

At the point of entry, samples were taken to measure AOC, TOC and UV254. For the first sampling date (11/18/02), samples were taken at all locations for measurements of TOC and UV254; however for subsequent dates, samples were only taken at the point of entry. Treated water AOC concentrations ranged from 107 to 253  $\mu\text{g/L}$  for all sampling dates. TOC concentrations ranged from 1.57 to 2.58  $\text{mg/L}$ . UV254 values ranged from 0.047 to 0.056  $\text{cm}^{-1}$ .

Temperature and pH were measured at all sampling locations for all sampling dates. pH values ranged from 7.45 to 8.40. Temperatures ranged from 15.6 to 27.8  $^{\circ}\text{C}$ . Temperatures on 11/18/02 ranged from 18.3 to 22.8  $^{\circ}\text{C}$ , decreased by 1/07/03 and had started to rise again by 4/08/03, with the highest temperatures occurring on 7/22/03 and 9/23/03.

Bromide measurements were made at several sampling locations for all sampling dates. Bromide concentrations ranged from 0.11 to 0.2 mg/L, with point of entry concentrations ranging from 0.12 to 0.18 mg/L. The highest bromide concentrations were measured from April to July.

Table 4.19  
pH, temperature and chlorine data for Utility D for 4/08/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
Site 1	18	7.9	0	3.4
Site 2	17	7.9	0	3.4
Site 3	17	7.9	0	3.5
Site 4	17	8.0	0	3.5
Site 5	18	8.0	0	3.7
Site 6	18	8.0	0	2.4
Site 7	19	7.9	0	2.8
Site 8	20	7.9	0	3.5
Site 9	20	7.9	0	3.4
Site 10	18	7.9	0	3.2
Site 11	17	8.0	0	3.3

Table 4.20  
Organic carbon, microbiological, nitrogen and bromide data for Utility D for 4/08/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)	Bromide (mg/L)
Site 1	253	1.92	0.047	5.05E+02	0.39	0.001	3.3	0.18
Site 2				6.50E+01	0.51	0.002	3.6	
Site 3				5.00E+01	0.49	0.006	3.0	0.17
Site 4				8.50E+01	0.51	0.005	3.6	
Site 5				3.00E+01	0.49	0.005	3.5	
Site 6				9.50E+01	0.51	0.021	3.6	
Site 7				9.00E+01	0.48	0.006	3.6	0.18
Site 8				6.00E+01	0.5	0	3.6	0.17
Site 9				4.50E+01	0.47	0.005	3.7	
Site 10				7.50E+01	0.5	0.007	3.6	0.18
Site 11				1.35E+02	0.49	0.003	3.6	0.18

Table 4.21

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility D for 4/08/03

Sample ID	$\text{CHCl}_3$	$\text{BrCl}_2\text{CH}$	$\text{Br}_2\text{ClCH}$	$\text{CHBr}_3$	THM4
Site 1	5	22	33	15	75
Site 2	5	22	33	15	75
Site 3	5	21	32	15	73
Site 4	5	21	33	15	75
Site 5	5	21	33	15	74
Site 6	5	22	33	15	76
Site 7	5	22	33	15	75
Site 8	6	22	34	15	77
Site 9	6	22	34	15	77
Site 10	5	21	33	16	75
Site 11	5	21	33	15	74

Table 4.22

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility D for 4/08/03

Sample ID	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	HAA9
Site 1	7	<2	4	6	8	2	6	6	3	43
Site 2	6	<2	4	6	9	2	7	6	3	43
Site 3	5	<2	4	6	9	2	7	6	3	41
Site 4	7	<2	4	6	9	3	7	6	3	45
Site 5	5	<2	4	6	9	2	6	6	3	42
Site 6	4	<2	4	6	9	2	7	6	3	42
Site 7	6	<2	4	6	8	3	7	6	3	44
Site 8	6	<2	4	6	9	2	7	6	3	43
Site 9	6	<2	4	6	9	3	6	6	3	42
Site 10	6	<2	4	6	9	3	7	6	3	44
Site 11	7	<2	3	6	9	3	7	6	3	44

Table 4.23

pH, temperature and chlorine data for Utility D for 1/07/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
Site 1	16	7.7	0.11	3.0
Site 2	16	7.7	0.16	2.1
Site 3	16	7.7	0.08	1.6
Site 4	16	7.9	0.08	2.1
Site 5	16	8.4	0.05	2.2
Site 6	16	8.1	0.09	2.0
Site 7	16	8.0	0.08	2.1
Site 10	17	7.4	0.03	0.1
Site 11	17	7.5	0.02	0.1
Site 14	16	7.5	0.04	0.6
Site 15	17	7.5	0.02	0.2
Site 16	17	7.3	0.04	0.1

Table 4.24

Organic carbon, microbiological, nitrogen and bromide data for Utility D for 1/07/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (mg/L)	NO <sub>3</sub> -N (mg/L)	Bromide (mg/L)
Site 1	188	1.70	0.056	<10	0.53	0.007	3.6	0.14
Site 2				1.4E+02	0.43	0.039	4.0	
Site 3				3.0E+01	0.47	0.011	3.7	
Site 4				8.0E+01	0.46	0.015	4.0	
Site 5				1.4E+02	0.49	0.017	3.4	
Site 6				3.5E+01	0.44	0.015	3.9	
Site 7				1.5E+02	0.43	0.016	4.0	0.14
Site 10				1.3E+03	0.1	0.135	3.8	0.09
Site 11				2.2E+03	0.09	0.114	3.6	0.08
Site 14				1.0E+03	0.07	0.046	3.8	0.10
Site 15				2.0E+03	0.11	0.180	4.9	0.12
Site 16				2.6E+03	0.09	0.244	4.8	

Table 4.25

Trihalomethane (THM) data (in µg/L) for Utility D for 1/07/03

Sample ID	CHCl <sub>3</sub>	BrCl <sub>2</sub> CH	Br <sub>2</sub> ClCH	CHBr <sub>3</sub>	THM4
Site 1	9	23	34	13	79
Site 2	9	22	33	13	77
Site 3	8	22	33	13	76
Site 4	8	22	33	13	75
Site 5	8	22	33	13	76
Site 6	8	22	32	13	74
Site 7	8	22	33	13	75
Site 10	8	13	16	6	43
Site 11	8	13	16	6	44
Site 14	10	16	20	8	53
Site 15	8	15	20	8	51
Site 16	8	13	17	6	44

Table 4.26

Haloacetic acid (HAA) data (in µg/L) for Utility D for 1/07/03

Sample ID	ClAA*	BrAA	Cl <sub>2</sub> AA	BrClAA*	Br <sub>2</sub> AA*	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
Site 1	16	<2	4	5	5	3	8	8	4	52
Site 2	<2	<2	4	6	7	3	8	8	4	39
Site 3	2	<2	4	6	7	3	8	7	5	42
Site 4	<2	3	4	6	8	3	9	8	5	45
Site 5	2	<2	4	6	7	3	8	8	5	43
Site 6	4	<2	4	6	7	3	8	8	4	45
Site 7	<2	<2	4	6	7	3	9	8	5	42
Site 10	<2	<2	<2	<2	<2	2	5	4	3	14
Site 11	<2	<2	<2	<2	<2	2	6	5	3	16
Site 14	<2	<2	<2	<2	<2	2	5	4	3	15
Site 15	<2	<2	<2	<2	<2	2	6	5	4	17
Site 16	<2	<2	<2	<2	<2	2	5	5	3	15

\*Matrix spike results did not meet QA/QC requirements; all other QA/QC requirements were met.

#### 4.4.3 Chlorine Residual and Heterotrophic Plate Counts

Results discussed in this section are intended to illustrate the effects of two of the four hydraulic scenarios encountered during this study. Sampling dates 4/8/03 and 1/7/03 provide a good contrast to demonstrate the role of different flow and demand patterns on the residence times and corresponding water quality characteristics at the different sampling locations. Results are first discussed for 4/08/03 and then for 1/07/03; Table 4.17 shows the corresponding residence times for each location for the two dates.

##### *Sampling date 4/08/03*

The total chlorine residual measured at the point of entry for sampling date 4/8/03 was 3.4 mg/L; a range of 2.4–3.7 mg/L was measured in the distribution system. Average residence times ranged from 0 to 14 hours. Figure 4.15 illustrates the relationship between residence time and total chlorine residual throughout this portion of Utility D's distribution system for samples taken on 4/08/03. Corresponding figures for the other sampling dates are presented in Appendix D. Total chlorine residual was fairly stable throughout this portion of the distribution system, given the relatively small change in residence times. The decrease in total chlorine residual at residence times of 6 and 13 hours may be due to interactions with the small diameter cast iron pipe at these locations. On all of the other sampling dates, there were marked losses in the chlorine residual at various sampling locations.

Despite the maintenance of a total chlorine residual in excess of 2.5 mg/L in this portion of the distribution system on 4/08/03, HPCs in the 10 to 1000 CFU/mL range were still detected (see Figure 4.16). Surprisingly, the highest HPCs were measured at the point of entry.

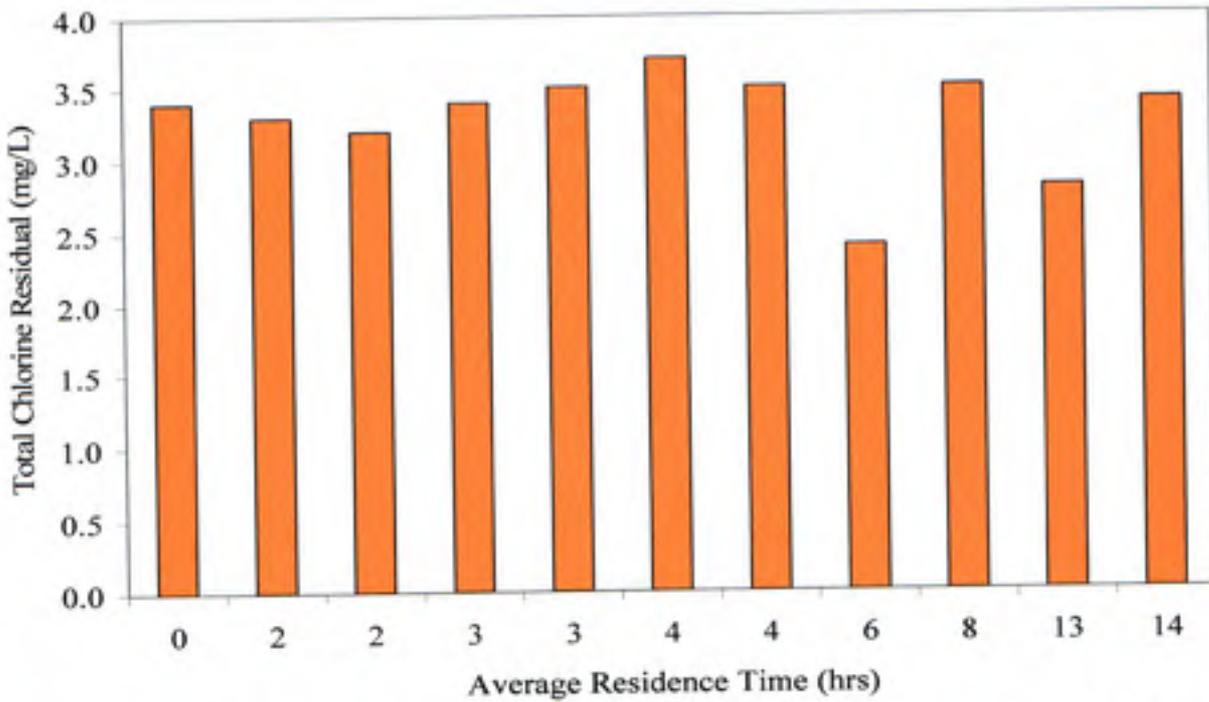


Figure 4.15 Total chlorine residual versus average residence time for Utility D for 4/08/03

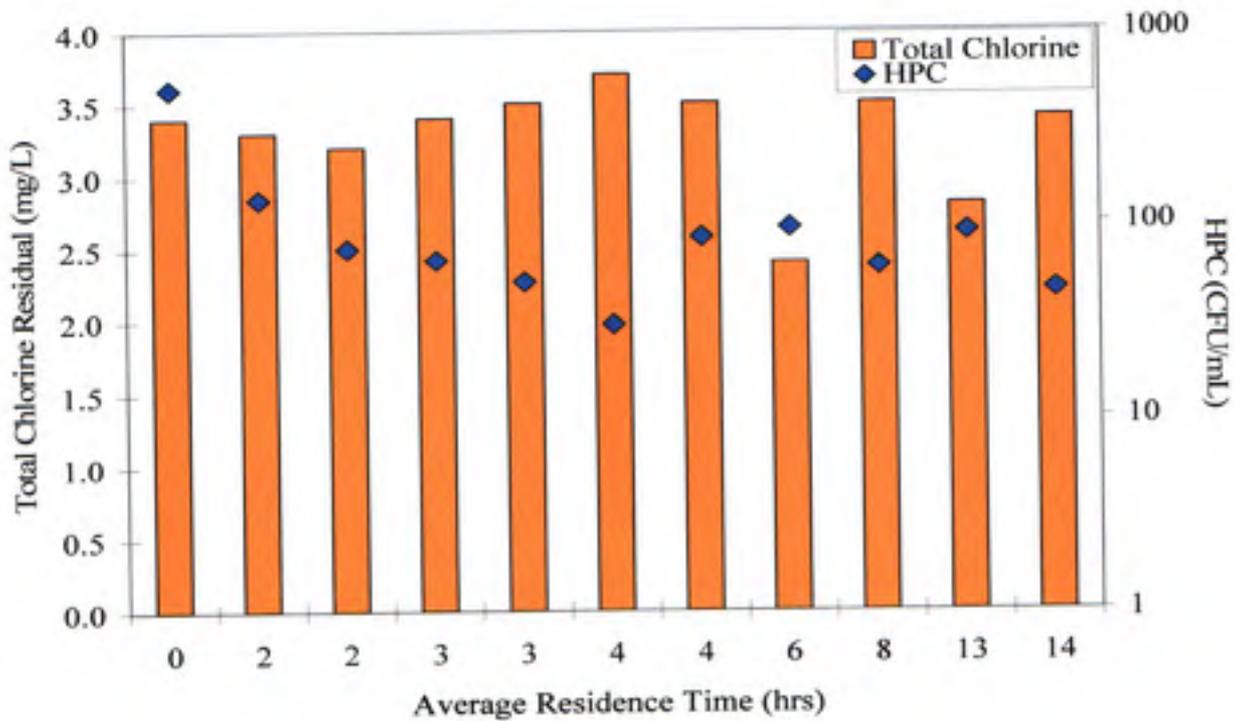


Figure 4.16 Total chlorine residual and HPC versus average residence time for Utility D for 4/08/03

*Sampling date 1/07/03*

The total chlorine residual measured at the point of entry for sampling date 1/07/03 was 3.0 mg/L; a range of 0.1–2.2 mg/L was measured in the distribution system. Average residence times on this sampling date ranged from 0 to 50 hours compared to 0 to 14 hours for 4/08/03. Figure 4.17 illustrates the relationship between residence time and total chlorine residual in this portion of Utility D's distribution system for samples taken on 1/07/03. As Figure 4.17 illustrates, the total chlorine residual was quite variable on this sampling date, in contrast to the stability shown in Figure 4.15 for sampling date 4/08/03. In particular, low residual chlorine conditions were encountered at residence times of 8, 11, 15, 37 and 50 hours. Similar difficulties in maintaining an appreciable total chlorine residual throughout the system were seen during the November, June and July samplings. Pipe material, which can be a factor in disinfectant decay, is not restricted to cast iron at these sampling locations.

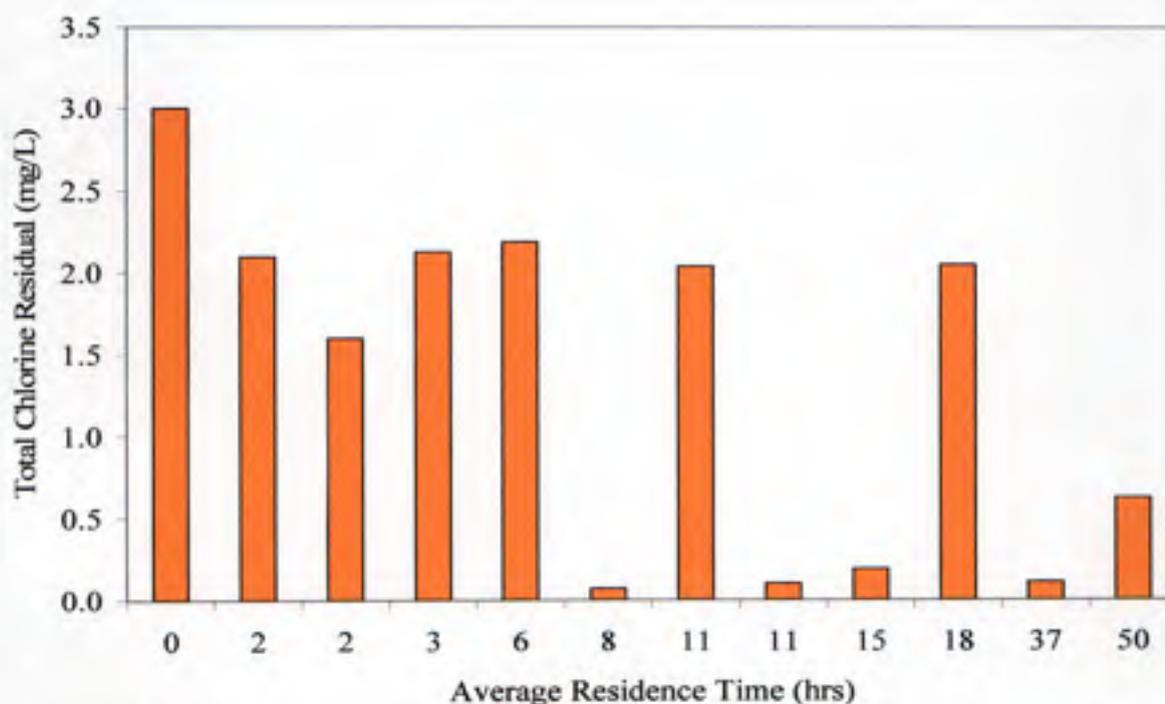


Figure 4.17 Total chlorine residual versus residence time for Utility D for 1/07/03

Figure 4.18 presents HPCs and total chlorine residual as residence time increases for sampling date 1/07/03. In contrast to the HPC results for 4/08/03, the decrease in total chlorine residual on 1/07/03 is associated with an increase in HPCs. The HPCs are highest at the locations with the lowest total chlorine residuals. This pattern is consistent with results obtained by Prevost et al. (1998) and Zhang and DiGiano (2002). The locations with residence times of 8, 11, 15, 37 and 50 hours have elevated HPCs in comparison to the rest of the sampling locations. HPCs at these residence times range between  $10^3$  and  $2.6 \times 10^3$  CFU/mL, in contrast to the rest of the sampling locations where HPCs range between  $< 10$  (point of entry) and  $1.5 \times 10^2$  CFU/mL. Similar results were found for the same sampling locations for the November sampling and similar results were seen on the June sampling. Increases in HPCs for the July sampling were also observed, but the counts were much lower, despite similar disinfectant residuals and warm weather temperatures.

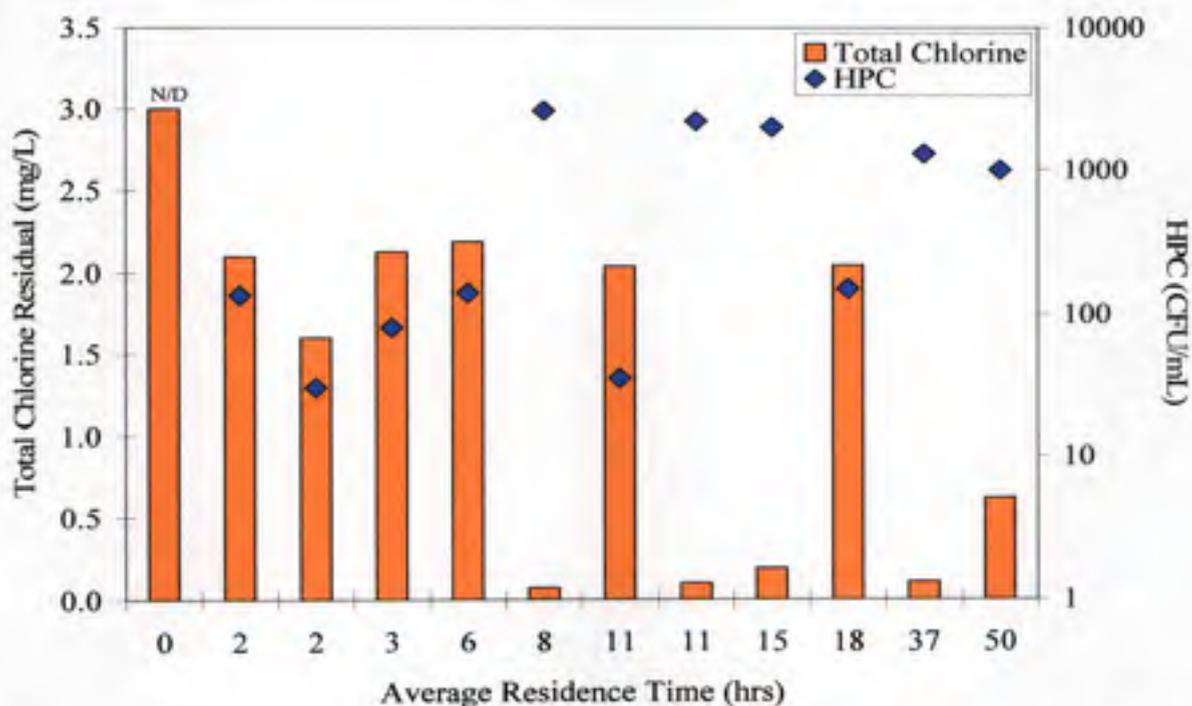


Figure 4.18 Total chlorine residual and HPC versus average residence time for Utility D for 1/07/03. (Heterotrophic Plate Count at the POE is  $< 10$  CFU/mL.)

#### 4.4.4 Disinfection By-Product Formation

##### *Trihalomethanes and Haloacetic Acids (4/08/03)*

Figure 4.19 presents THM4 concentration and speciation as residence time increases for sampling conducted on 4/08/03. Corresponding figures for the other sampling dates are presented in Appendix D. As noted above (see Table 4.20), the source water for Utility D contains appreciable levels of bromide. Bromine-containing compounds comprise an average of 93% of the THM4 concentration, by weight, for the sampling on 4/0/03; bromodichloro- and dibromochloromethane ( $\text{CHBrCl}_2$  and  $\text{CHBr}_2$ , respectively) are the primary THM4 species.

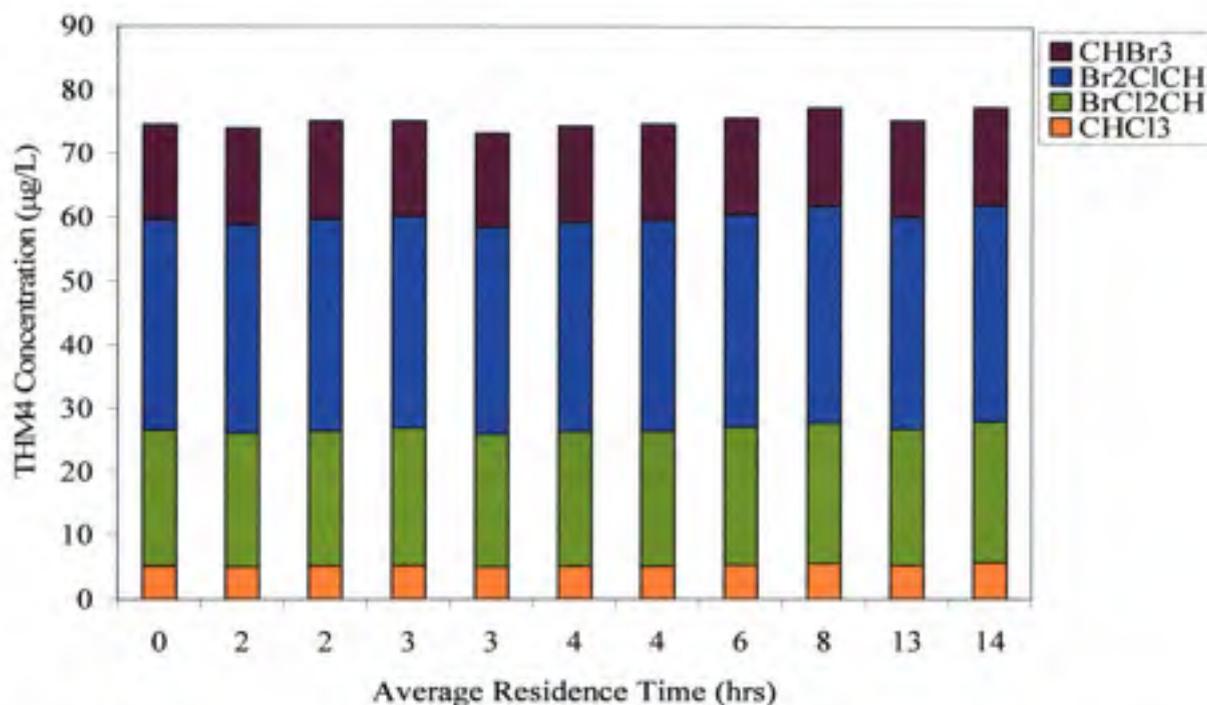


Figure 4.19 THM4 concentration versus average residence time for Utility D for 4/08/03

THM4 concentrations remain stable as residence time increases, despite a minor decrease in total chlorine residual at some locations, confirming that monochloramine stops subsequent THM4 formation. This is consistent with theory and with the literature (Johnson and Jensen 1986, Norton and LeChevallier 1997) and is not surprising in view of the relatively small change in residence times for this date. Similar results were seen for sampling date 9/23/03, although

bromine-containing compounds comprised a smaller percentage of the THM4 concentration. No sampling location exceeded the 80 µg/L MCL for THM4 during the 4/08/03 sampling event.

Figure 4.20 presents HAA9 concentration and speciation as residence time increases for sampling conducted on 4/08/03. Corresponding figures for the other sampling dates are presented in Appendix D. Bromine-containing compounds comprised, on average, 72% of HAA9, by weight, at each sampling location. All nine species are represented except bromoacetic acid (BrAA) whose concentration was below the detection limit. Like THM4, HAA9 concentrations remained stable as residence time increased despite the minor reduction in total chlorine residual.

Figure 4.21 presents THM4 and HAA9 data together for 4/08/03. Chloramines have been shown to increase DBP concentrations minimally throughout distribution systems (Wolfe, Ward and Olson 1984; Johnson and Jensen 1986; Stevens, Moore and Miltner 1989; Norton and LeChevallier 1997; Pope et al. 2002). Thus, the results presented in Figure 4.21 are consistent with results found in the literature although, again, this is not surprising in view of the small change in residence times. Similar trends were seen for sampling date 9/23/03. No sampling location exceeded the 60 µg/L MCL for HAA5 on sampling date 4/08/03.

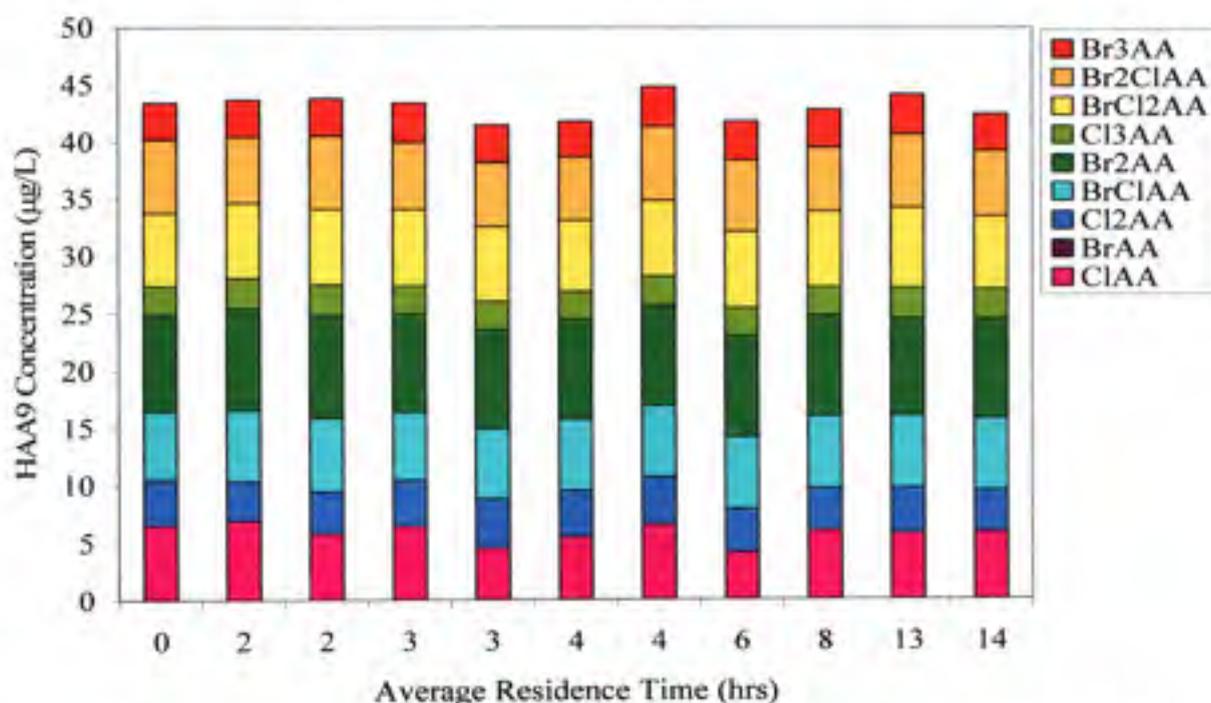


Figure 4.20 HAA9 concentration versus average residence time for Utility D for 4/08/03

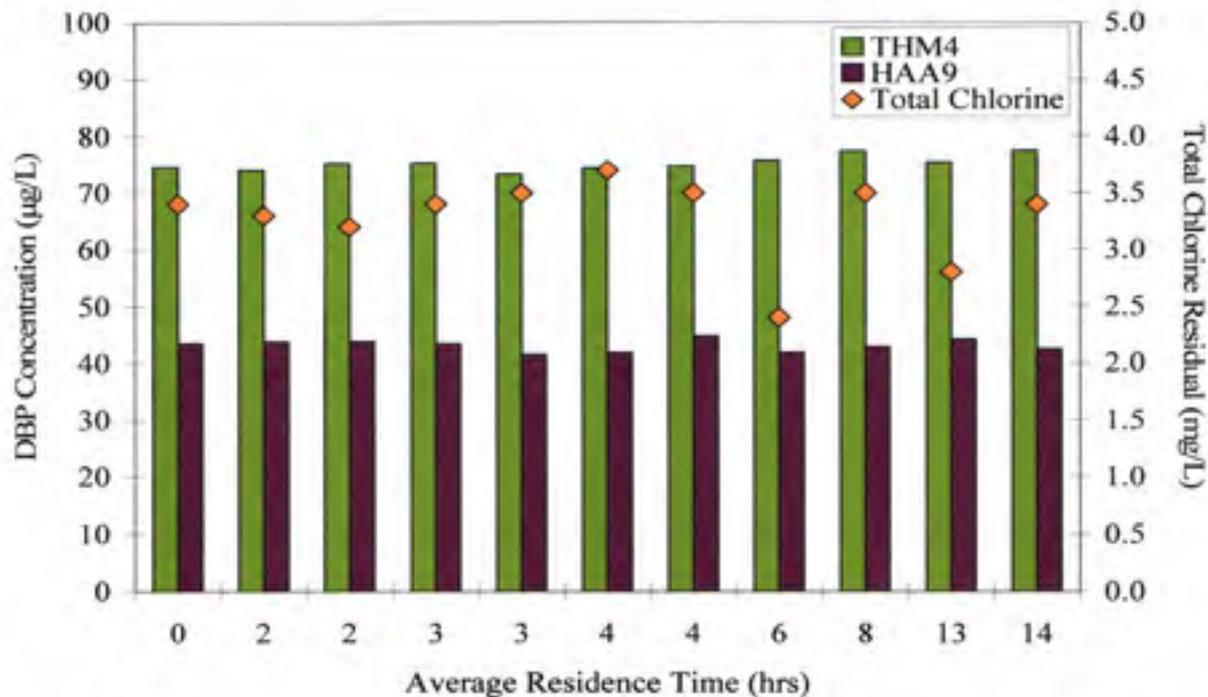


Figure 4.21 THM4, HAA9 concentrations and total chlorine residual versus average residence time for Utility D for 4/08/03

#### *Trihalomethanes and Haloacetic Acids (1/07/03)*

Figure 4.22 presents THM4 concentrations and total chlorine residual as residence time increases and Figure 4.23 shows the corresponding THM4 speciation as residence time increases for sampling conducted on 1/07/03. In contrast to sampling date 4/08/03, THM4 concentrations did not remain constant but decreased at the five locations exhibiting reduced chlorine concentrations, i.e. residence times of 8, 11, 15, 37 and 50 hours. Similar patterns were seen for the November and June samplings. THM4 concentrations for the July sampling, remained stable despite a decrease in total chlorine residual at the same locations. The distribution of THM species was essentially the same at locations with appreciable chlorine residuals and at locations with reduced chlorine residuals. The reason for the decreased THM4 concentrations is not clear. There is no evidence in the literature suggesting biodegradation of THMs in the absence of a chlorine residual as there is for HAAs, except under anoxic conditions (Singer et al. 1993), which is not likely the case here.

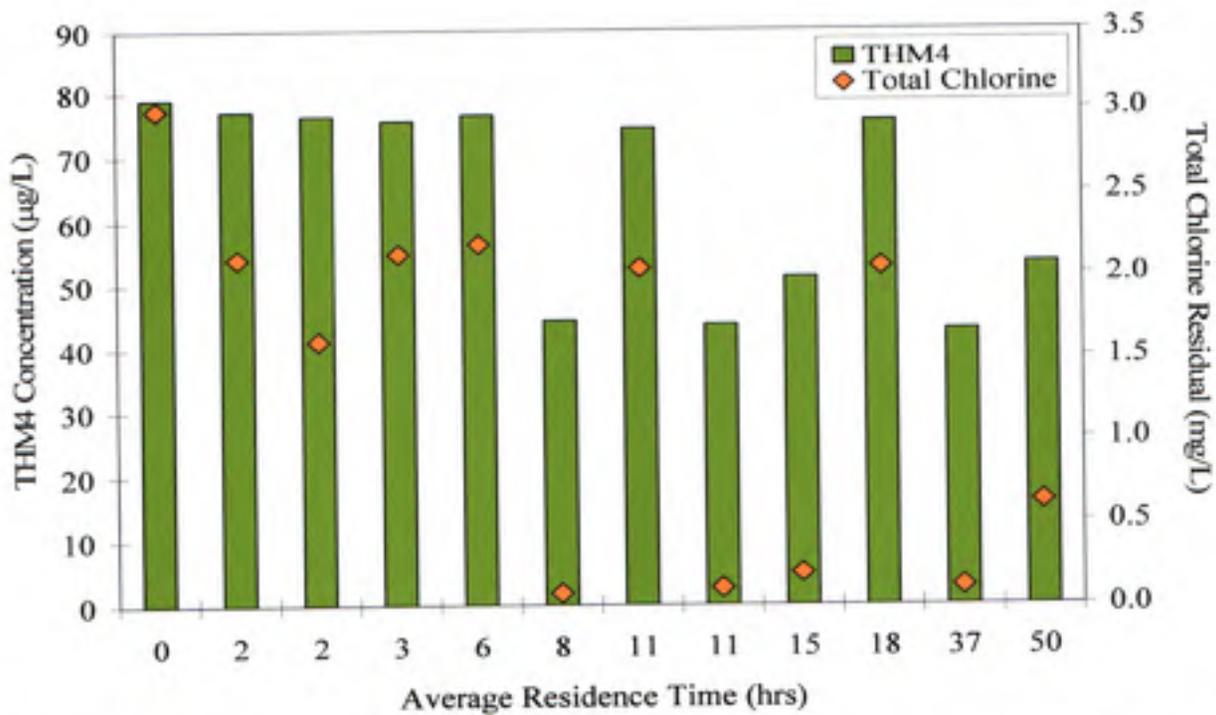


Figure 4.22 THM4 and total chlorine residual versus average residence time for Utility D for 1/07/03

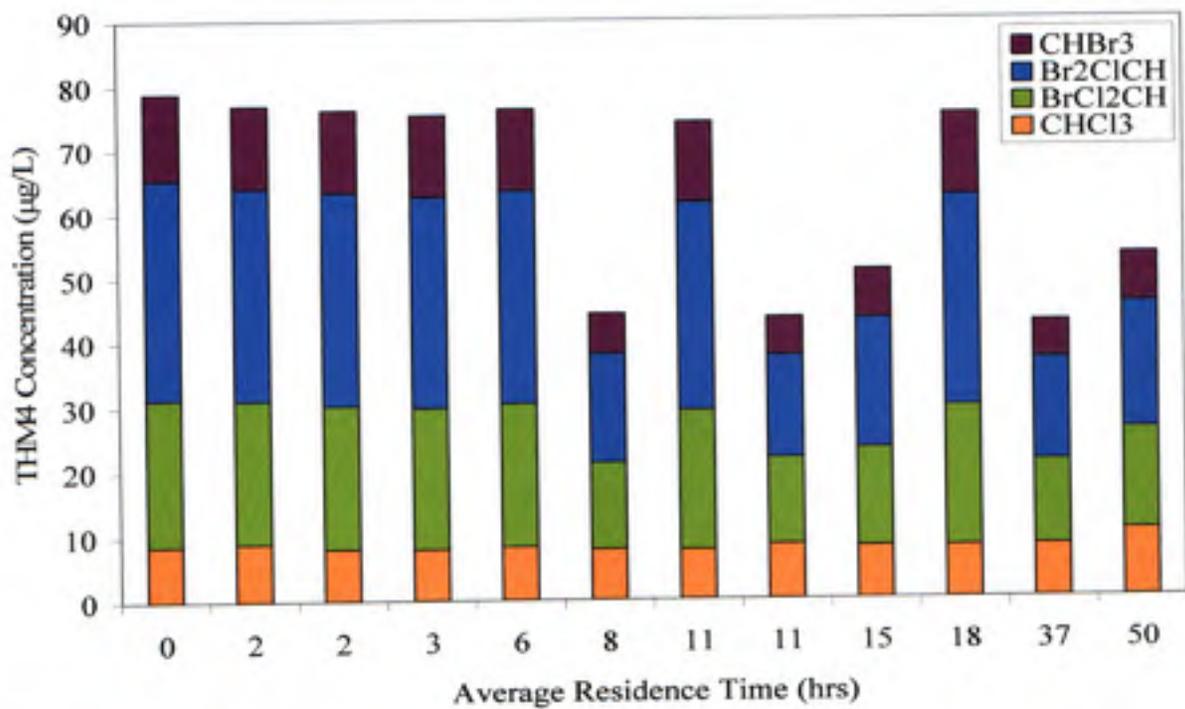


Figure 4.23 THM4 speciation versus residence time for Utility D for 1/07/03

Figure 4.24 presents HAA9 concentrations and total chlorine residual as residence time increases and Figure 4.25 presents HAA9 speciation as residence time increases for sampling conducted on 1/07/03. As with the THM4 concentrations, and in contrast to the 4/08/03 sampling, HAA9 concentrations do not remain constant but decrease at the locations with reduced chlorine residuals, i.e. at residence times of 8, 11, 15, 25, 37 and 50 hours. This occurs at the same locations that exhibited a decrease in THM4 concentrations. This trend was observed for two of the other sampling dates when a loss in total chlorine residual was observed, i.e. in November and June. However, as with the THMs, HAA9 concentrations did not decrease during the July sampling despite measured losses in total chlorine residual. It should be noted (see Figure 4.25) that the decreased HAA9 concentration at residence times of 8, 11, 15, 25, 37 and 50 hours are due to a loss in the mono- and dihaloacetic acids. The trihaloacetic acids are the only remaining HAA species. This is consistent with the literature which reports that microorganisms tend to degrade the mono- and dihaloacetic acid species but not the trihaloacetic acid species (van der Ploeg, van Hall and Janssen 1991; Williams, Williams and Gordon 1995).

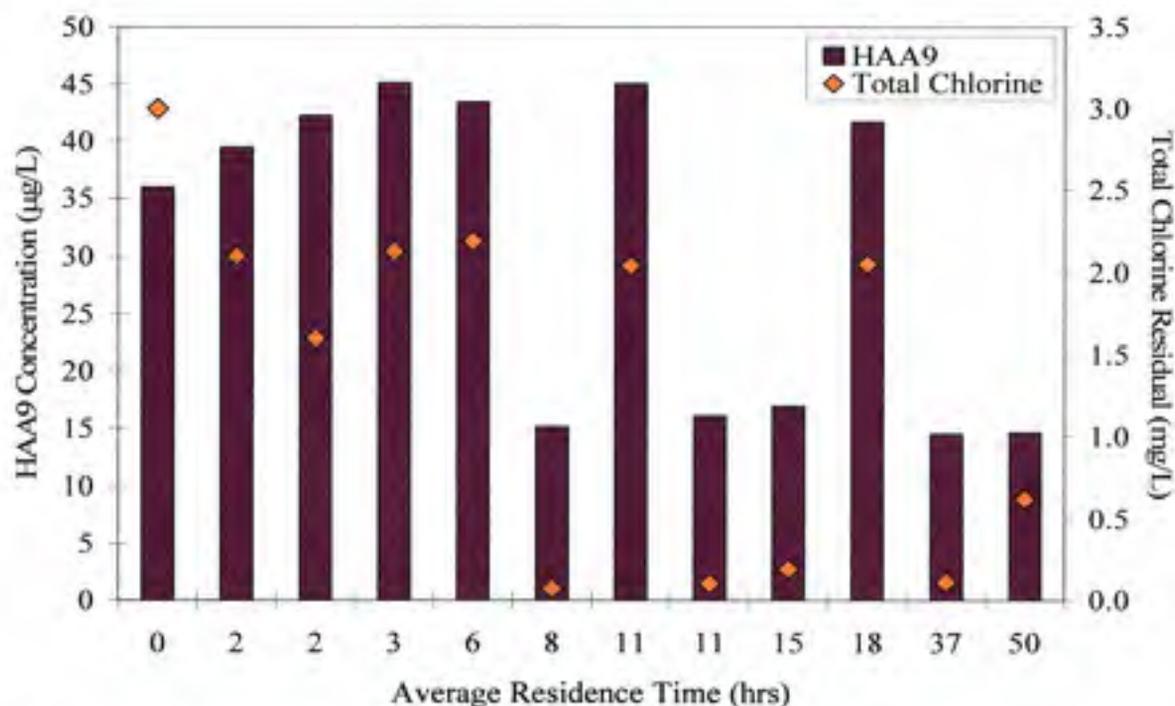


Figure 4.24 HAA9 and total chlorine residual versus average residence time for Utility D for 1/07/03

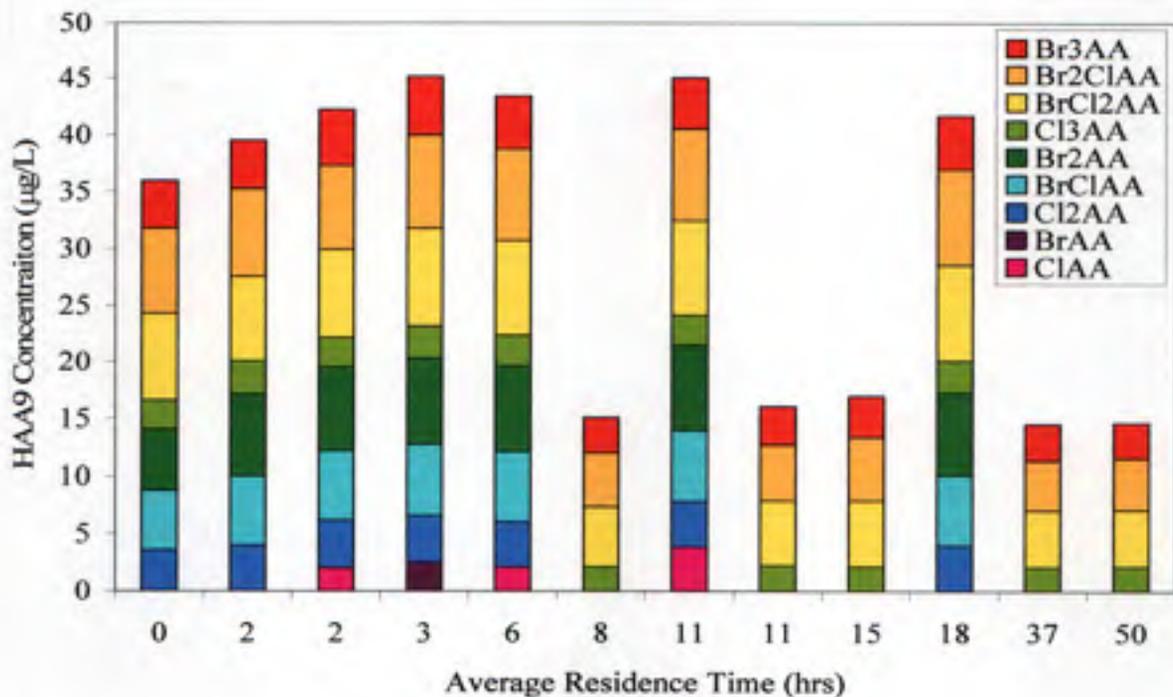


Figure 4.25 HAA9 speciation versus residence time for Utility D for 1/07/03

Figures 4.26 and 4.27 present both THM4 and HAA9 results with increasing residence time and increasing total chlorine concentration, respectively, for sampling date 1/07/03. Decreases in the THM4 concentrations correspond with decreases in the HAA9 concentrations, though there does not seem to be a correlation with residence time. There is, however, an association between decreases in THM4 and HAA9 concentrations and decreases in total chlorine residual. Biodegradation of HAAs in the absence of a high chloramine residual is a logical explanation for the HAA9 decrease, because the more readily degradable HAA species are the ones that exhibit a reduced concentration. No explanation is available for the decrease in THM concentrations at these same locations.

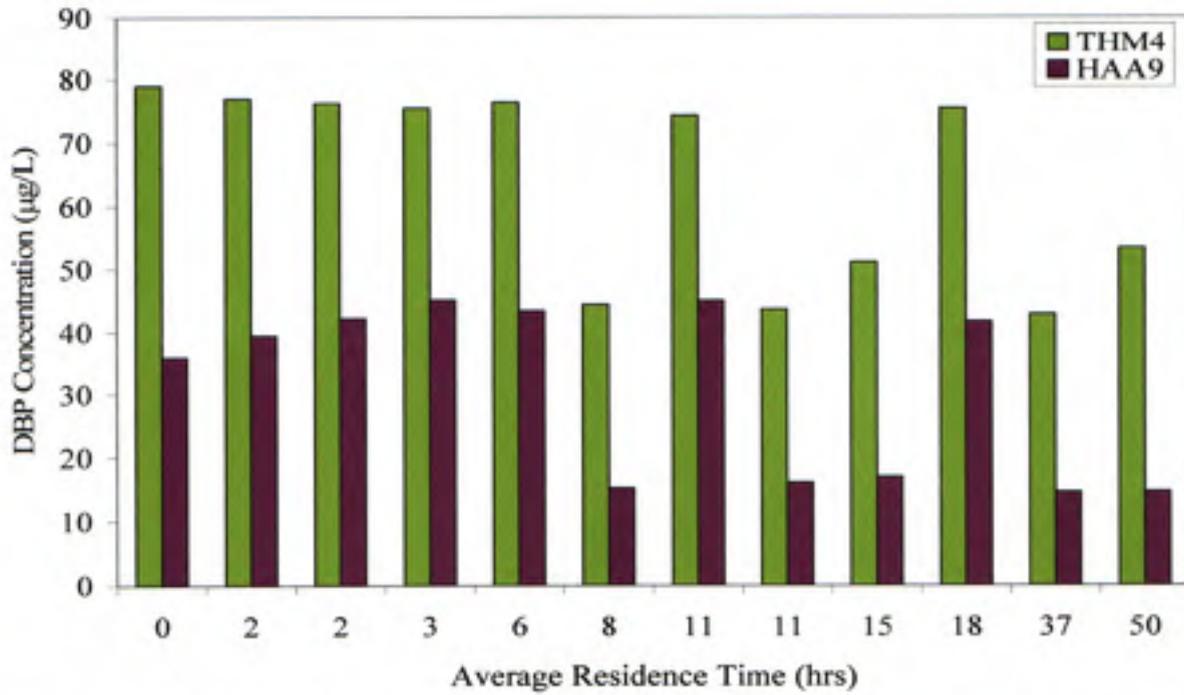


Figure 4.26 THM4 and HAA9 concentration versus average residence time for Utility D for 1/07/03

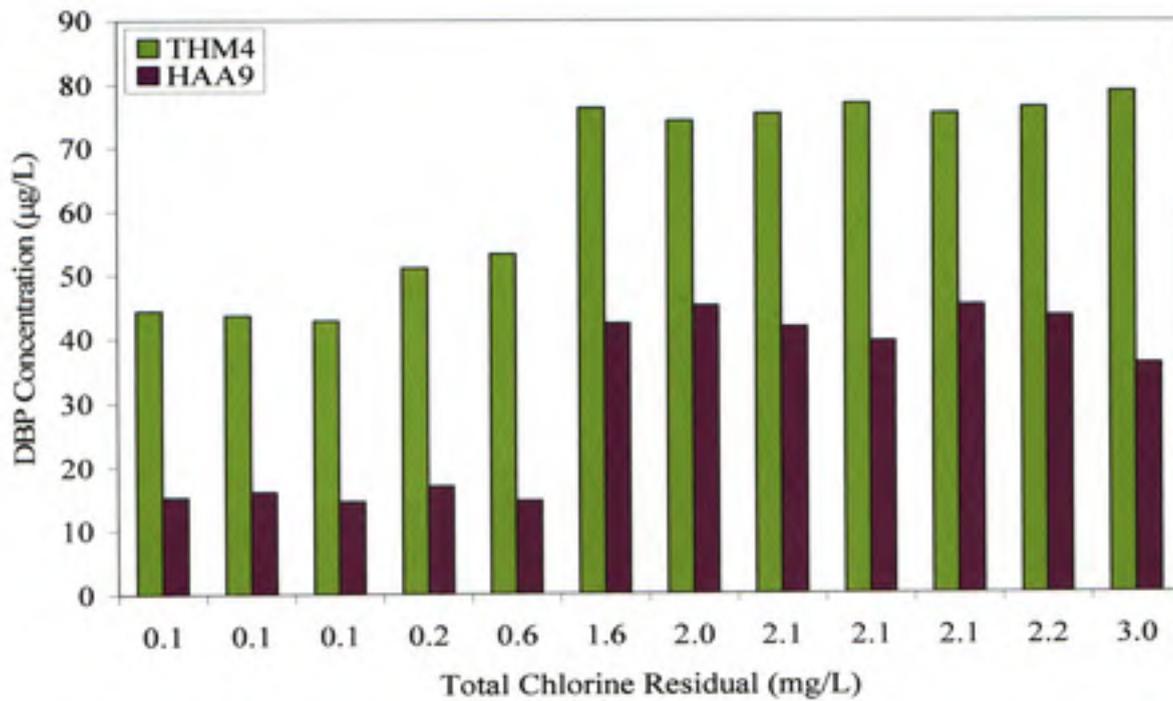


Figure 4.27 THM4 and HAA9 concentration versus total chlorine residual for Utility D for 1/07/03

#### 4.4.5 Nitrification

Nitrate measurements made at the point of entry indicate that nitrate was present in the source water at concentrations ranging from 2.4 to 3.6 mg/L for all sampling dates. Increases in nitrate or nitrite concentrations and loss of ammonia in the distribution system may be indicators of nitrification.

*Sampling date 4/08/03*

Figure 4.28 presents ammonia, nitrate and nitrite concentrations with increasing residence time for 4/08/03. Corresponding figures for the other sampling dates are presented in Appendix D. No evidence of nitrification is apparent for the 4/08/03 results, most likely because of the persistence of a relatively high and consistent combined chlorine residual in this portion of the system. A similar pattern was observed during the July and September sampling events, despite a reduction in the total chlorine residual at several sampling locations.

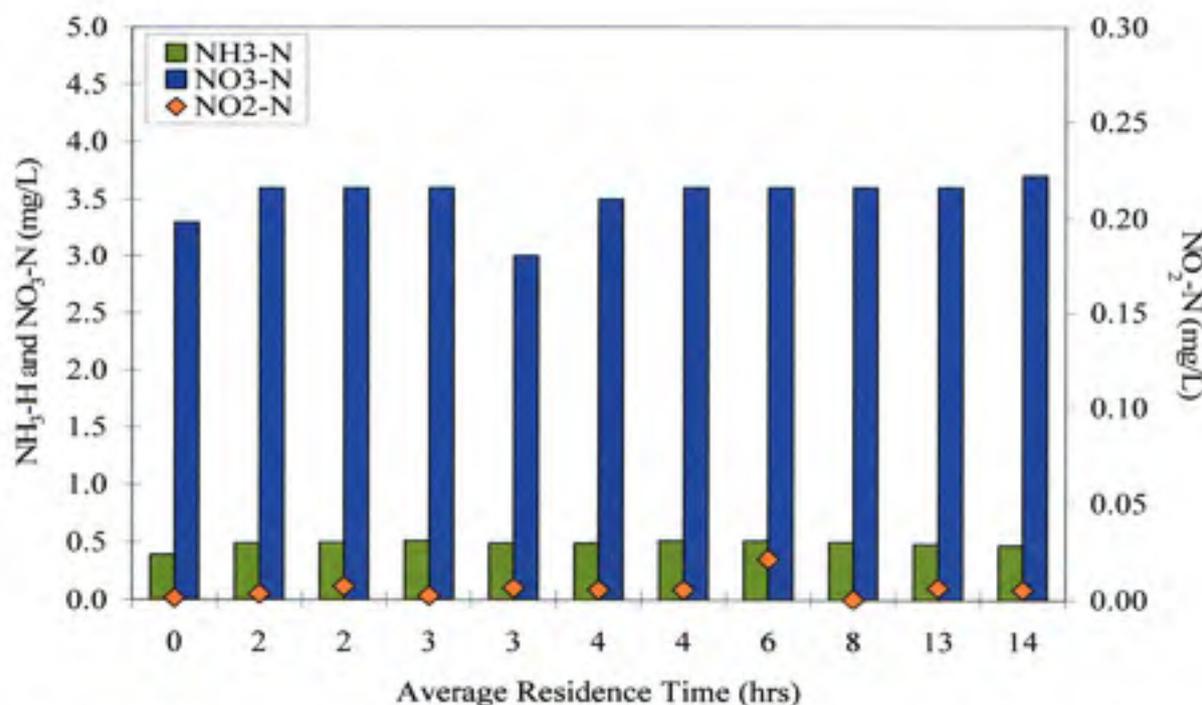


Figure 4.28 Nitrogen species versus average residence time for Utility D for 4/08/03

Sampling date 1/07/03

Figure 4.29 presents ammonia, nitrate and nitrite concentrations with increasing residence time for 1/07/03. Appreciable decreases in chlorine residuals were noted on this date (see Figure 4.17). Nitrification, as evidenced by a decrease in ammonia concentrations and an increase in nitrite and nitrate concentrations, was observed at residence times of 8, 11, 15, 37 and 50 hours. These correspond to the locations with a significant loss in total chlorine residual (see Figure 4.30). From the point of entry concentrations to those sampling locations where nitrification is observed, nitrate concentrations increased up to 1.3 mg/L as N, nitrite concentrations increased between 0.039 and 0.237 mg/L as N and ammonia concentrations decreased between 0.42 and 0.46 mg/L as N. Given the relatively low concentrations, this is not an unreasonable mass balance on N. Results for sampling dates 11/18/02 and 6/10/03 exhibited the same evidence of nitrification. Incomplete nitrification, i.e. the oxidation of ammonia to nitrite, can be an issue because nitrite exerts a high chlorine demand (5 mg/L of chlorine of  $\text{Cl}_2$  for 1 mg/L of nitrite as N) (Skadsen 1993). Results presented in Figure 4.30 corroborate results found in the literature.

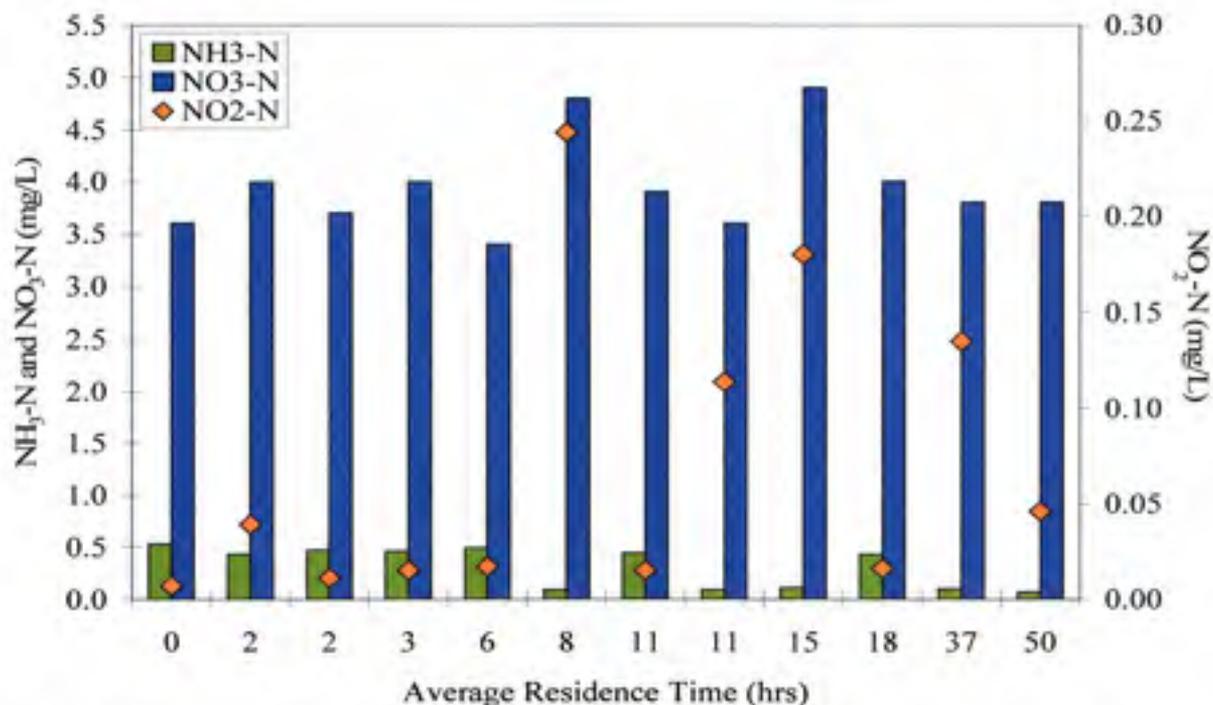


Figure 4.29 Nitrogen species versus average residence time for Utility D for 1/07/03

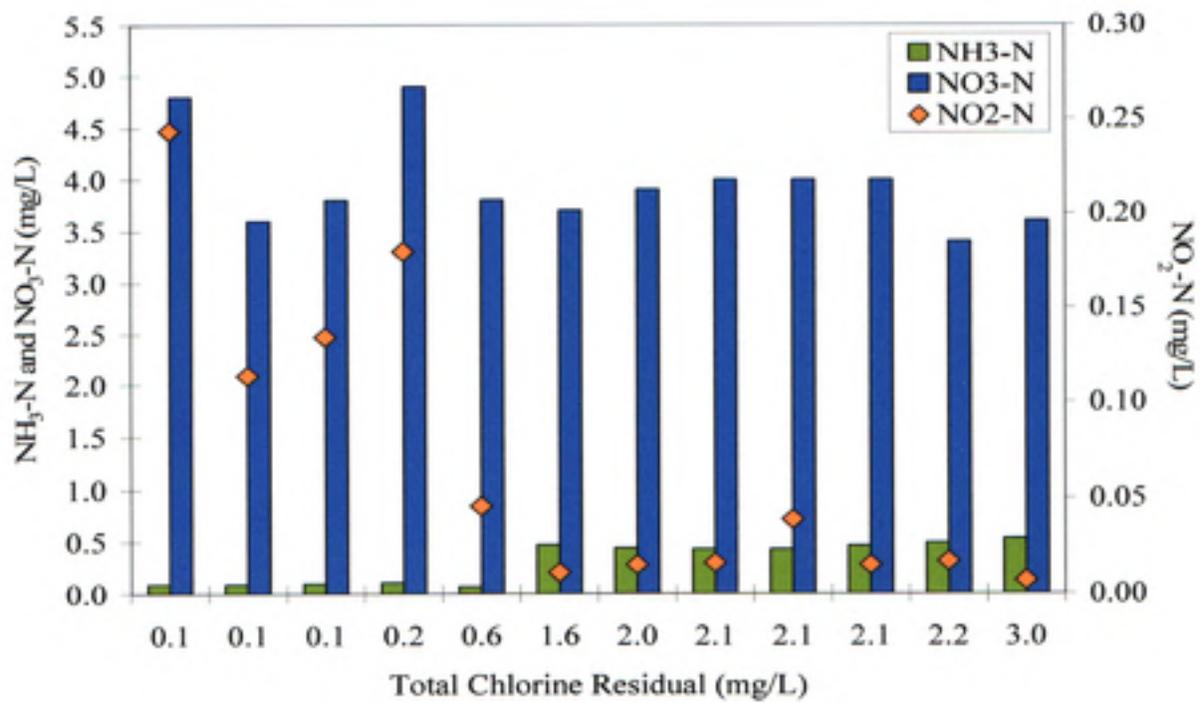


Figure 4.30 Nitrogen species versus total chlorine residual for Utility D for 1/07/03

#### 4.5 SUMMARY

Utility A and Utility B utilized free chlorine as a secondary disinfectant. Sampling results showed that chlorine residual decreased as residence time increased; this trend was significant for Utility A, but occurred to a lesser degree for Utility B. In addition, at both utilities, THM4 and HAA9 concentrations increased as residence time increased. HAA9 concentrations were somewhat more variable throughout the Utility B distribution system, while evidence of HAA biodegradation was observed at Utility A at high residence times. At Utility A, loss of chlorine residual and decreases in HAA9 concentration were coupled with increases in HPCs at high residence times.

Utilities C and D utilized chloramines as their secondary disinfectant. Data obtained for Utility C showed that the disinfectant residual remained constant throughout the distribution system, except at sampling locations where evidence of nitrification and biodegradation of HAAs was observed. For Utility D, depending on the hydraulic scenario, the stability of the total chlorine residual changed. For some scenarios, the total chlorine residual remained constant while, for others, a significant decrease in total chlorine residual was observed. The change in hydraulic scenarios changed the average residence times at each location. THM4 and HAA9 concentrations remained constant at both utilities when the disinfectant residual remained constant. However, a decrease in HAA9 concentrations was seen at both utilities, at those sampling locations that showed a decrease in total chlorine residual and high HPCs, consistent with a biodegradation mechanism. A decrease in THM4 concentrations was seen in the Utility D system, at the same locations where HAA9 biodegradation occurred. An explanation for this phenomenon is not available at this time. Evidence of nitrification was seen at both utilities, specifically at locations with low total chlorine residual.

Figure 4.31, a summary figure, was created to investigate the association between the decrease in chlorine residual and the increase in HPC for all utilities for all sampling dates. An exponential relation between the free chlorine residual and HPCs is shown. The R2 value for the exponential relationship is low, indicating a weak association between the loss of chlorine residual and the increase in HPC, although there does seem to be a pattern of HPCs decreasing with increasing chlorine residual. It is difficult to distinguish between the effects of free and combined chlorine residual on HPCs from these data.

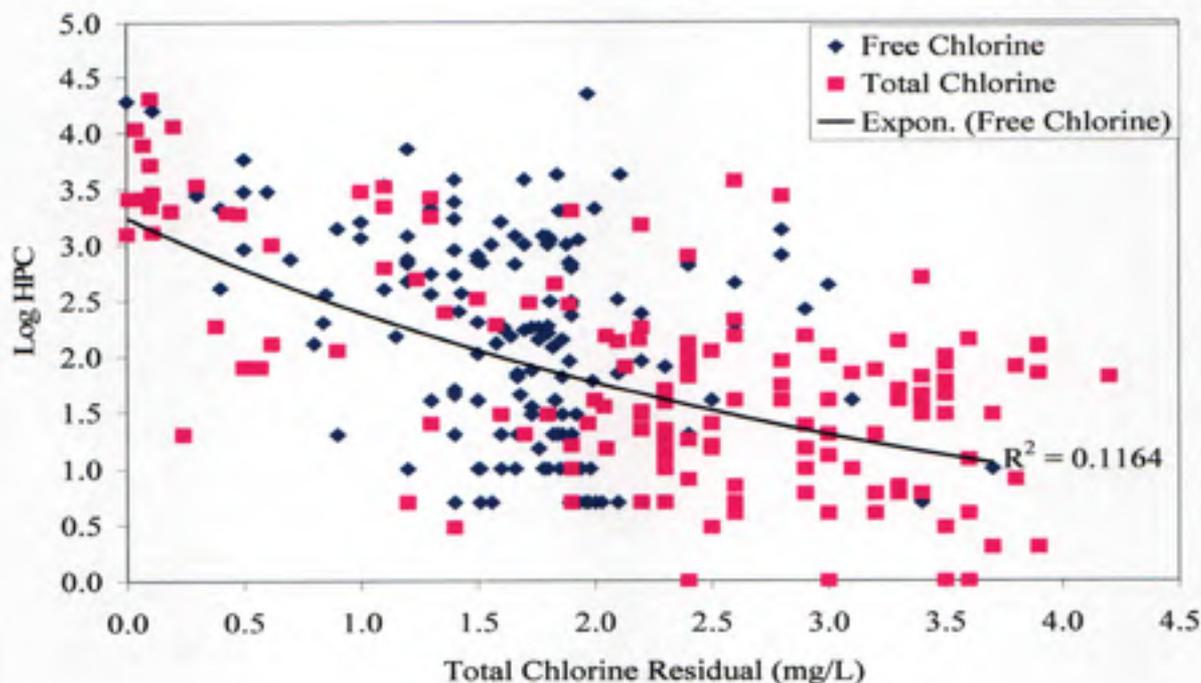


Figure 4.31 Chlorine residual and HPC for all utilities for all sampling dates.

A cursory review of the impact of pipe material and pipe diameter on DBP formation, speciation and decay was performed for all utilities. Little evidence, with the exceptions noted in the text, was found to indicate that pipe material and pipe diameter affected the quality of the water found in the distribution systems of the participating utilities.

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

The goal of this study was to evaluate the formation and decay of THMs and HAAs in finished drinking water in four distribution systems with respect to residence time and secondary residual type and concentration, and to determine the occurrence of other phenomena, such as the incidence of nitrification and elevated HPCs, which may affect the quality of finished drinking water. Based on the data collected during this project, the following conclusions can be reached:

1. Dissipation of the free chlorine residual was observed as residence time increased for those utilities (A and B) that utilized free chlorine as a secondary disinfectant. Free chlorine continued to react with available TOC in the finished water and with the walls of the pipes and materials on those walls, resulting in higher THM and HAA concentrations and decreased chlorine residual as residence time increased.
2. For those utilities (C and D) that utilized chloramines as a secondary disinfectant, the chloramine residual was observed to be relatively stable as residence time increased. Under certain operating scenarios for Utility D, the residence time at many of the sampling locations increased appreciably and the total chlorine residual decreased to very low levels at several sampling locations. When the total chlorine residual was maintained at both utilities, there was little formation of THMs or HAAs in the distribution system.
3. A decrease in the concentration of HAAs was observed at several locations for three of the four utilities (A, C and D). Two of the utilities utilized chloramines as their secondary disinfectant and one utilized free chlorine. These decreases were observed at locations with low chlorine residuals and, in most cases, high residence times. The decrease in HAA concentration is believed to be a result of biodegradation. Free chlorine residuals at Utility B were relatively high throughout the system preventing biodegradation of HAAs.
4. Evidence of nitrification was observed in both of the chloraminated distribution systems. This evidence consisted of decreased levels of ammonia in correspondence with increased concentrations of nitrate and nitrite. For Utility C, the most noticeable evidence

of nitrification occurred at locations with the highest residence times. For Utility D, evidence of nitrification was observed only on those occasions when the distribution system operated under certain hydraulic scenarios that resulted in longer residence times and appreciable decreases in total chlorine residual.

5. Despite the presence of a measurable total chlorine residual, HPCs on the order of  $10^2$ - $10^4$  were measured in all of the distribution systems. Elevated HPCs were seen in some distribution systems despite the presence of 1.5 mg/L of free chlorine.
6. No impact of pipe diameter or pipe material on DBP formation, loss in chlorine residual, elevated HPCs, or incidence of nitrification could be discerned.

## 5.2 RECOMMENDATIONS

This study attempted to characterize temporal effects, such as seasonal temperature changes but it did not address what happens to DBPs on a short-term, diurnal basis. Temporal studies to evaluate the effects of diurnal variations in system operations on DBP concentrations would be useful to more definitively determine the formation and decay of DBPs in distribution systems and the impact of changes in flow and demand on other related water quality parameters.

As evidenced by this study, maximum HAA and THM concentration do not always occur at the same location. This is particularly significant in light of the proposed Stage II D/DBP Rule that will require utilities to sample at locations of maximum DBP concentrations. This and other studies have shown that, in systems with free chlorine, THM concentrations tend to increase as residence time increases, and in chloraminated systems, THMs remain relatively constant. However, several studies, including this one, have shown that biodegradation of HAAs can occur in distribution systems that use either free chlorine or chloramines as a secondary disinfectant when that disinfectant is depleted. Biodegradation of HAAs can change the location of maximum HAA concentration so that it is different than the location of maximum THM concentration. A tool or guidance to aid utilities in determining their locations of maximum DBP concentrations would be useful for all utilities that will be required to comply with the Stage II D/DBP Rule.

While many utilities use chloramines to control the subsequent formation of DBPs in the distribution system, the use of chloramines is not without problems. Both utilities that utilized chloramines in this study experienced nitrification. Investigations into the causes of nitrification, whether the loss of disinfectant residual promotes the growth of nitrifying bacteria and/or whether the growth of nitrifying bacteria promotes the loss of chloramine residual, would be highly useful for those utilities that have problems with nitrification.

Finally, investigation of the cause of the decrease in THM concentrations at locations with low chlorine residuals (and at locations where decreased HAA concentrations occur), such as that seen at several locations for Utility D should be conducted. This phenomenon has been seen at other utilities, although it is not widely reported and there have been no system-wide studies to understand its cause.

## REFERENCES

- Backer, L. C., D. L. Ashley, M. A. Bonin, F. L. Cardinali, S. M. Kieszak and J. V. Wooten. 2000. Household Exposures to Drinking Water Disinfection By-Products: Whole Blood Trihalomethane Levels. *Journal of Exposure and Analysis and Environmental Epidemiology*, 10:321-326.
- Baribeau, H. S., S. W. Krasner, R. Chinn and P. C. Singer. 2000. Impact of Biomass on the Stability of Haloacetic Acids in Trihalomethanes in a Simulated Distribution System. *In Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Baribeau, H. S., M. Prevost, R. Desjardins and P. Lafrance. 2001. Changes in Chlorine and DOX Concentrations in Distribution Systems. *Journal of American Water Works Association*, 93(12):102-114.
- Bellar, T. A., J. J. Lichtenberg and R. C. Kroner. 1974. The Occurrence of Organohalides in Chlorinated Drinking Water. *Journal of American Water Works Association*, 66(12):703-706.
- Boulos, L., H. S. Baribeau, P. C. Singer, S. L. Williams, R. Gullick, S. A. Schlesinger and C. Nichols. 2003. Formation and Decay of THMs and HAAs in Distribution Systems: Results of Five Case Studies. *In Proceedings AWWA Water Quality & Technology Conference*. Denver, Colo.: AWWA.
- Bove, F. J., M. C. Fulcomer, J. B. Klotz, J. Esmart, E. M. Dufficy and J. E. Savrin. 1995. Public Drinking Water Contamination and Birth Outcomes. *American Journal of Epidemiology*, 141(9):850-862.
- Brophy, K. S., H. S. Wienberg and P. C. Singer. 2000. Quantification of Nine Haloacetic Acids Using Gas Chromatography with Electron Capture Detection. *In Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water*. Edited by S. E. Barrett, S. Krasner and G. Amy. Oxford University Press.

- Camper, A. K. 2003. Factors Influencing Microbial Water Quality in Distribution Systems. *In Proceedings AWWA Annual Conference*. Denver, Colo.: AWWA.
- Cantor, K. P., C. F. Lynch, M. E. Hildesheim, M. Dosemeci, J. Lubin, M. Alavanja and G. Craun. 1998. Drinking Water Source and Chlorination By-Products: Risk of Bladder Cancer. *Epidemiology*, 9(1):21-28.
- Chen, W. J. and C. P. Wiesel. 1998. Halogenated DBP Concentrations in a Distribution System. *Journal of American Water Works Association*, 90(4):151-163.
- Clark, R. M., R. C. Thurnau, M. Sivaganesan and P. Ringhand. 2001. Predicting the Formation of Chlorinated and Brominated By-Products. *Journal of Environmental Engineering*, 127(6):493-501.
- Cowman, G. and P. C. Singer. 1996. Effect of Bromide Ion on Haloacetic Acid Speciation Resulting from Chlorination and Chloramination of Aquatic Humic Substances. *Environmental Science & Technology*, 30(1):16-24.
- Croue, J. P., J. F. Debroux, G. Aiken, J. A. Leenbeer and G. L. Amy. 1999. Natural Organic Matter: Structural Characteristics and Reactive Properties. *Formation and Control of Disinfection By-Products in Drinking Water*. Edited by P. C. Singer. Denver, CO: AWWA.
- Cunliffe, D. A. 1991. Bacterial Nitrification in Chloraminated Water Supplies. *Applied and Environmental Microbiology*, 57(11):3399-3402.
- Dickenson, E., L. Work and R. S. Summers. 2002. Short-Term Chlorine Decay and Disinfection By-Product Formation. *In Proceedings AWWA Annual Conference*. Denver, Colo.: AWWA.
- Dodds, L., W. King, C. Woolcott and J. Pole. 1999. Trihalomethanes in Public Water Supplies and Adverse Birth Outcomes. *Epidemiology*, 10(3):233-237.

- Duirk, S. E., J. C. Whitney and R. L. Valentine. 2002. Preliminary Investigations into Chloramine Loss and DBP Formation in the Presence of NOM and Bromide. *In Proceedings AWWA Annual Conference*. Denver, Colo.: AWWA.
- Gallard, H. and U. von Guten. 2002. Chlorination of Natural Organic Matter: Kinetics of Chlorination and of THM Formation. *Water Research*, 36(1):65-74.
- Harrington, G. W., D. R. Noguera, A. I. Kandou and D. J. Vanhoven. 2002. Pilot-Scale Evaluation of Nitrification Control Strategies. *Journal of American Water Works Association*, 94(11):78-89.
- Hildesheim, M. E., K. P. Cantor, C. F. Lynch, M. Dosemeci, J. Lubin, M. Alavanja and G. Craun. 1998. Drinking Water Source and Chlorination By-Products: Risk of Colon and Rectal Cancers. *Epidemiology*, 9(1):29-35.
- Johnson, J. D. and J. N. Jensen. 1986. THM and TOX Formation: Routes, Rates and Precursors. *Journal of American Water Works Association*, 78(4):156-161.
- Kiene, L., W. Lu and Y. Levi. 1998. Relative Importance of the Phenomena Responsible for Chlorine Decay in Drinking Water Distribution Systems. *Water Science and Technology*, 38(6):219-227.
- Krasner, S. W., M. J. Scilimenti, R. Chinn, Z. K. Chowdhury and D. M. Owen. 1996. The Impact of TOC and Bromide on Chlorination By-Product Formation. *Disinfection By-Products in Water Treatment*. Edited by R. A. Minear and G. L. Amy. Chelsea, Mich.: Lewis Publishers.
- LeBel, G. L., F. M. Benoit and D. T. Williams. 1997. A One-Year Study of Halogenated Disinfection By-Products in the Distribution System of Treatment Plants Using Three Different Disinfection Processes. *Chemosphere*, 34(11):2301-2317.
- LeChevallier, M. W., C. D. Cawthon and R. G. Lee. 1988. Factors Promoting Survival of Bacteria in Chlorinated Water Supplies. *Applied and Environmental Microbiology*, 54(3):649-654.

- LeChevallier, M. W., C. D. Cawthon and R. G. Lee. 1988b. Inactivation of Biofilm Bacteria. *Applied and Environmental Microbiology*, 54(10):2492-2499.
- LeChevallier, M. W., C. D. Lowry and R. G. Lee. 1990. Disinfecting Biofilms in a Model Distribution System. *Journal of American Water Works Association*, 82(7):87-99.
- LeChevallier, M. W., C. D. Lowry, R. G. Lee and D. L. Gibbon. 1993. Examining the Relationship Between Iron Corrosion and the Disinfection of Biofilm Bacteria. *Journal of American Water Works Association*, 85(7):111-123.
- LeChevallier, M. W., N. J. Welch and D. B. Smith. 1996. Full-Scale Studies of Factors Related to Coliform Regrowth in Drinking Water. *Applied and Environmental Microbiology*, 62(7):2201-2211.
- Liang, L. and P. C. Singer. 2003. Factors Influencing the Formation and Relative Distribution of Haloacetic Acids and Trihalomethanes Under Controlled Chlorination Conditions. *Environmental Science & Technology*, 37(13):2920-2928.
- Lieu, N. I., R. L. Wolfe and E. G. Means, III. 1993. Optimizing Chloramine Disinfection for the Control of Nitrification. *Journal of American Water Works Association*, 85(2):84-90.
- Lu, W., L. Kiene and Y. Levi. 1999. Chlorine Demand of Biofilms in Water Distribution Systems. *Water Research*, 33(3):827-835.
- McRae, B. M., T. M. LaPlara and R. M. Hozalski. 2004. Biodegradation of Haloacetic Acids by Bacterial Enrichment Cultures. *Chemosphere*, Article in Press
- Meyer, I., T. Francais, B. Lykins, M. Dutang and P. Hartemann. 1993. Influence of Biofilm on Disinfection By-Products in a Distribution Network. *Water Supply*, 11(3/4):355-364.
- Momba, M. N. B., S. Ndaliso and M. A. Binda. 2003. Effect of a Combined Chlorine-Monochloramine Process on the Inhibition of Biofilm Regrowth in Potable Water Systems. *Water Science and Technology: Water Supply*, 3(1-2):215-221.

- NCI. 1976. *Report on the Carcinogenesis Bioassay of Chloroform*. NTIS PB-264-018. National Cancer Institute, Bethesda, MD.
- Norton, C. D. and M. W. LeChevallier. 1997. Chloramination: Its Effect on Distribution System Water Quality. *Journal of American Water Works Association*, 89(7):66-77.
- Odell, L. H., G. J. Kirmeyer, A. Wilczak, J. G. Jacangelo, J. P. Marcinko and R. L. Wolfe. 1996. Controlling Nitrification in Chloraminated Systems. *Journal of American Water Works Association*, 88(7):86.
- Peters, C. J., R. J. Young and R. Perry. 1980. Factors Influencing the Formation of Haloforms in the Chlorination of Humic Materials. *Environmental Science & Technology*, 14(11):1391-1395.
- Pintar, K. D. M. and R. M. Slawson. 2003. Effect of Temperature and Disinfection Strategies on Ammonia-oxidizing Bacteria in a Bench-scale Drinking Water Distribution System. *Water Research*, 37(8):1805-1817.
- Pope, P. G., G. E. Speitel, Jr., M. Martin-Doole and R. Collins. 2002. Factors Contributing to DXAA Formation During Chloramination. In *Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Prevost, M., A. Rompre, J. Coallier, P. Servais, P. Laurent, B. Clement and P. Lafrance. 1998. Suspended Bacterial Biomass and Activity in Full-Scale Drinking Water Distribution Systems: Impact of Water Treatment. *Water Research*, 32(5):1393-1406.
- Reckhow, D. A., P. C. Singer and R. L. Malcolm. 1990. Chlorination of Humic Materials: Byproduct Formation and Chemical Interpretations. *Environmental Science & Technology*, 24(11):1655-1664.
- Regan, J. M., G. W. Harrington, H. S. Baribeau, R. De Leon and D. R. Noguera. 2003. Diversity of Nitrifying Bacteria in Full-Scale Chloraminated Distribution Systems. *Water Research*, 37(1):197-205.

- Rodriguez, M. J., J.-B. Serodes, J. Pitre and M. Huard. 2002. Seasonal Variations of Trihalomethanes and Haloacetic Acids within Water Distribution Systems: A Case Study in Quebec (Canada). *In Proceedings AWWA Annual Conference*. Denver, Colo.: AWWA.
- Romppe, A., M. Prevost, J. Coallier, P. Brisebois and J. Lavoie. 2000. Impacts of Implementing a Corrosion Control Strategy on Biofilm Growth. *Water Science and Technology*, 41(4-5):287.
- Rook, J. J. 1974. Formation of Haloforms During Chlorination of Natural Waters. *Water Treatment and Examination*, 23(2):234-243.
- Rossman, L. A., R. A. Brown, P. C. Singer and J. R. Nuckols. 2001. DBP Formation Kinetics in a Simulated Distribution System. *Water Research*, 35(14):3483-3489.
- Savitz, D. A., K. W. Andrews and L. M. Pastore. 1994. Drinking Water and Pregnancy Outcome in Central North Carolina: Source, Amount and Trihalomethane Levels. *Environmental Health Perspectives*, 103(6):592-596.
- Singer, P. C. 1993. Disinfection By-Products in U.S. Drinking Waters: Past, Present and Future. *In Proceedings National Conference on Environmental Engineering*.
- Singer, P. C., R. D. G. Pyne, M. AVS, C. T. Miller and C. Mojonnier. 1993b. Examining the Impact of Aquifer Storage and Recovery on DBPs. *Journal of American Water Works Association*, 85(11):85-94.
- Singer, P. C. 1994. Control of Disinfection By-Products in Drinking Water. *Journal of Environmental Engineering*, 120(4):727-744.
- Singer, P. C. 1999. Humic Substances as Precursors for Potentially Harmful Disinfection By-Products. *Water Science and Technology*, 40(9):25-30.
- Singer, P. C. 2001. Variability and Assessment of Disinfection By-Product Concentrations in Water Distribution Systems. *Microbial Pathogens and Disinfection By-Products in Drinking Water: Health Effects and Management Risks*. Edited by G. F. Craun, F. S. Hauchman and D. E. Robinson. Washington, DC: International Life Sciences.

- Singer, P. C. 2002. Occurrence of Haloacetic Acids in Chlorinated Drinking Water. *Water Science and Technology: Water Supply*, 2(5):487-492.
- Singer, P. C., E. DePaz, D. L. Ashley, B. Blount, J. R. Nuckols, C. R. Wilkes, D. Cade, C. Lyu, S. Gordon, J. Masters and M. Brinkman. 2003. Impact of Trihalomethane Concentrations in Tap Water and Water Use Activities on Biological Levels of Trihalomethanes. *In Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Skadsen, J. 1993. Nitrification in a Distribution System. *Journal of American Water Works Association*, 85(7):95-103.
- Skadsen, J. 2002. Effectiveness of High pH in Controlling Nitrification. *Journal of American Water Works Association*, 94(7):73-83.
- Standard Methods for the Examination of Water and Wastewater*. 20th Edition. 1998. L. A. Clesceri, A. E. Greenberg and A. D. Eaton. Washington, DC: APHA, AWWA and WEF.
- Stevens, A. A., L. A. Moore and R. J. Miltner. 1989. Formation and Control of Non-Trihalomethane Disinfection By-Products. *Journal of American Water Works Association*, 81(8):54-60.
- Symons, J. M., S. W. Krasner, M. J. Scilimenti, L. A. Simms, H. W. Sorenson, Jr., G. E. Speitel, Jr. and A. C. Diehl. 1996. Influence of Bromide Ion on Trihalomethane and Haloacetic Acid Formation. *Disinfection By-Products in Water Treatment*. Edited by R. A. Minear and G. L. Amy. Boca Raton: Lewis Publishers.
- Symons, J. M., G. E. Speitel, Jr., C. J. Hwang, S. W. Krasner, S. E. Barrett, A. C. Diehl and R. Xia. 1998. Factors Affecting Disinfection By-Product Formation During Chloramination. *In Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- USEPA. 1979. National Interim Primary Drinking Water Regulation: Control of Trihalomethanes in Drinking Water. *Federal Register*, 63:94:69390.
- USEPA. 1991. National Primary Drinking Water Regulations: Final Rule. *Federal Register*, 56:20:3526.

- USEPA. 1995. *Methods for the Determination of Organic Compounds in Drinking Water - Supplement III*. EPA/600/R-95-131. Cincinnati, Ohio.
- USEPA. 1998. Stage I Disinfectants and Disinfection By-Products: Final Rule. Federal Register, 63:241:69389.
- USEPA. 2000. The History of Drinking Water Treatment. EPA-816-F-00-006. <http://www.epa.gov/safewater/consumer/hist.pdf>.
- USEPA. 2003. Stage II Disinfectants and Disinfection By-Products: Proposed Rule. Federal Register, 68:159:49548.
- van der Ploeg, J., G. van Hall and D. B. Janssen. 1991. Characterization of the Haloacid Dehalogenase from *Xanthobacter autotrophicus* GJ10 and Sequencing of the *dh1B* Gene. *Journal of Bacteriology*, 173:7925-7933.
- Vasconcelos, J. J., L. A. Rossman, W. M. Grayman, P. F. Boulos and R. M. Clark. 1997. Kinetics of Chlorine Decay. *Journal of American Water Works Association*, 89(7):54-65.
- Vikesland, P. J., K. Ozekin and R. L. Valentine. 1998. Effect of Natural Organic Matter on Monochloramine Decomposition: Pathway Elucidation through the Use of Mass and Redox Balances. *Environmental Science & Technology*, 32(10):1409-1416.
- Vikesland, P. J., K. Pzekin and R. L. Valentine. 2001. Monochloramine Decay in Model and Distribution System Waters. *Water Research*, 35(7):1766-1776.
- Waller, K., S. H. Swan, G. DeLorenze and B. Hopkins. 1998. Trihalomethanes in Drinking Water and Spontaneous Abortion. *Epidemiology*, 9(2):134-140.
- Wilczak, A., J. G. Jacangelo, J. P. Marcinko, L. H. Odell, G. J. Kirmeyer and R. L. Wolfe. 1996. Occurrence of Nitrification in Chloraminated Distribution Systems. *Journal of American Water Works Association*, 88(7):74-85.

- Williams, S. L., R. L. Williams and A. S. Gordon. 1995. Degradation of Haloacetic Acids (HAA) at Maximum Residence Time Locations (MRTLs). *In Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Williams, S. L., R. L. Williams and A. S. Gordon. 1996. The Impact of Bacterial Degradation of Haloacetic Acids (HAA) in the Distribution System. *In Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Williams, S. L., R. L. Williams and J. Yuan. 1998. Bacterial Degradation of Haloacetic Acids in the Distribution System. *In Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Williams, S. T., R. L. Williams and D. F. Rindfleisch. 1994. Deadend on Haloacetic Acids. *In Proceedings AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Wolfe, R. L., N. R. Ward and B. H. Olson. 1984. Inorganic Chloramines as Drinking Water Disinfectants: A Review. *Journal of American Water Works Association*, 76(5):74-84.
- Zhang, W. and F. A. DiGiano. 2002. Comparison of Bacterial Regrowth in Distribution Systems Using Free Chlorine and Chloramine: A Statistical Study of Causative Factors. *Water Research*, 36(6):1469-1482.

**APPENDIX A**  
**Utility C**

Table A.1

pH, temperature and chlorine data for Utility C for 10/15/02

Sample ID	Temperature		Total Cl <sub>2</sub> (mg/L)
	(°C)	pH	
POE	22	7.5	4.0
1	22	7.2	3.3
2	23	7.3	3.0
3	24	7.2	3.5
4	23	7.2	2.5
8	24	7.2	2.6
9	23	7.3	3.0
10	23	7.2	3.3
13	23	7.2	3.3
20	25	7.3	0.5
15	24	7.3	2.2
1721	23	7.0	2.4

Table A.2

Organic carbon, microbiological and nitrogen data for Utility C for 10/15/02

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE		3.10	0.048	0.0E+00	0.532	0.99	<0.020
1		2.55	0.045	0.0E+00	0.500	<0.50	0.031
2		2.94	0.047	1.0E+02	0.717	1.58	<0.020
3		2.69	0.050	3.0E+01	0.672	3.68	<0.020
4		2.92	0.049	1.1E+02	0.753	1.87	0.026
8		2.74	0.045	2.1E+02	0.699	8.51	0.033
9		2.80	0.047	4.0E+01	0.631	1.18	<0.020
10		2.85	0.048	5.0E+01	0.522	0.76	<0.020
13		2.58	0.047	0.0E+00	0.536	<0.50	0.028
20		3.08	0.044	8.0E+01	0.695	8.81	0.022
15		2.73	0.037	1.5E+03	0.135	461.8	0.068
1721		2.63	0.043	1.3E+02	0.601	3.62	0.028

Table A.3

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility C for 10/15/02

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
POE	6	14	23	13	56
1	7	19	27	17	70
2	7	18	29	18	72
3	8	20	30	18	76
4	7	19	29	18	73
8	7	19	29	17	72
9	7	18	28	17	70
10	7	18	27	17	69
13	7	18	27	16	68
20	8	18	25	14	65
15	7	19	30	17	73
1721	6	16	24	14	60

Table A.4

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility C for 10/15/02

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
POE	5	9	3	9	7	2	6	4	2	47
1	4	3	7	15	12	3	8	8	3	63
2	5	8	6	14	12	3	10	8	4	70
3	2	6	6	13	11	3	8	8	3	60
4	3	7	9	12	11	3	8	7	3	63
8	2	3	9	18	14	4	13	12	5	80
9	2	3	6	13	11	3	8	7	3	56
10	<2	2	7	14	11	3	9	8	3	57
13	<2	2	6	13	11	3	8	7	3	53
20	<2	3	8	16	13	3	9	8	3	63
15	2	1	7	11	10	3	6	6	2	48
1721	5	7	2	14	12	3	9	8	4	64

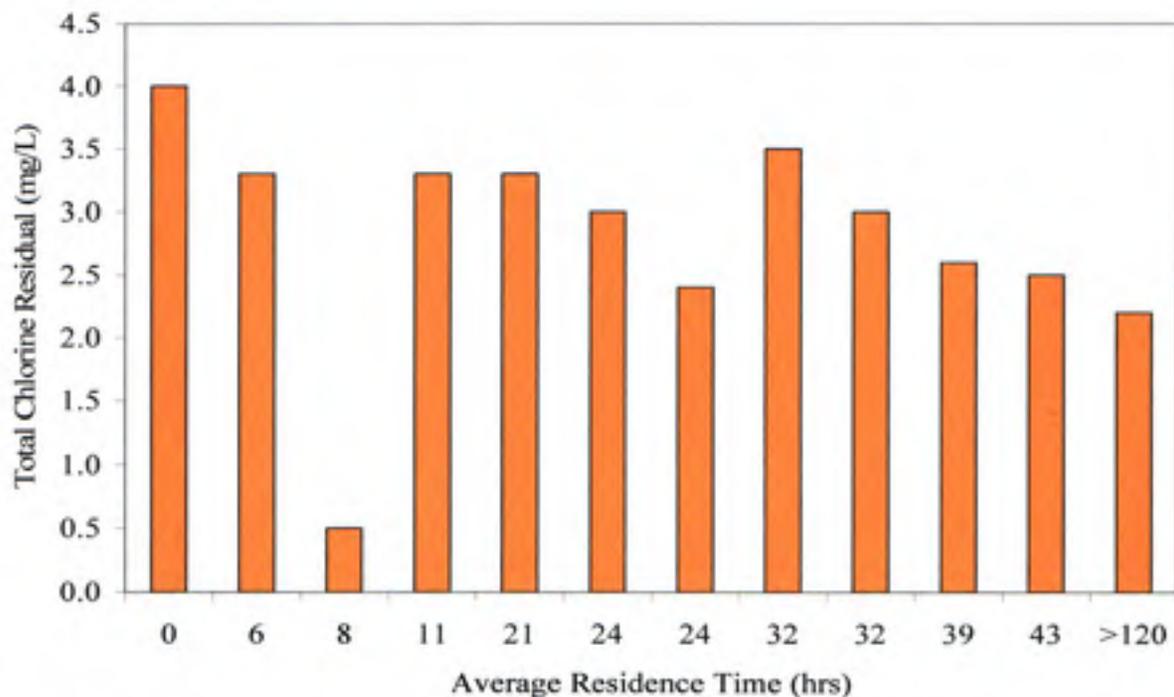


Figure A.1 Total chlorine residual versus average residence time for Utility C for 10/15/02

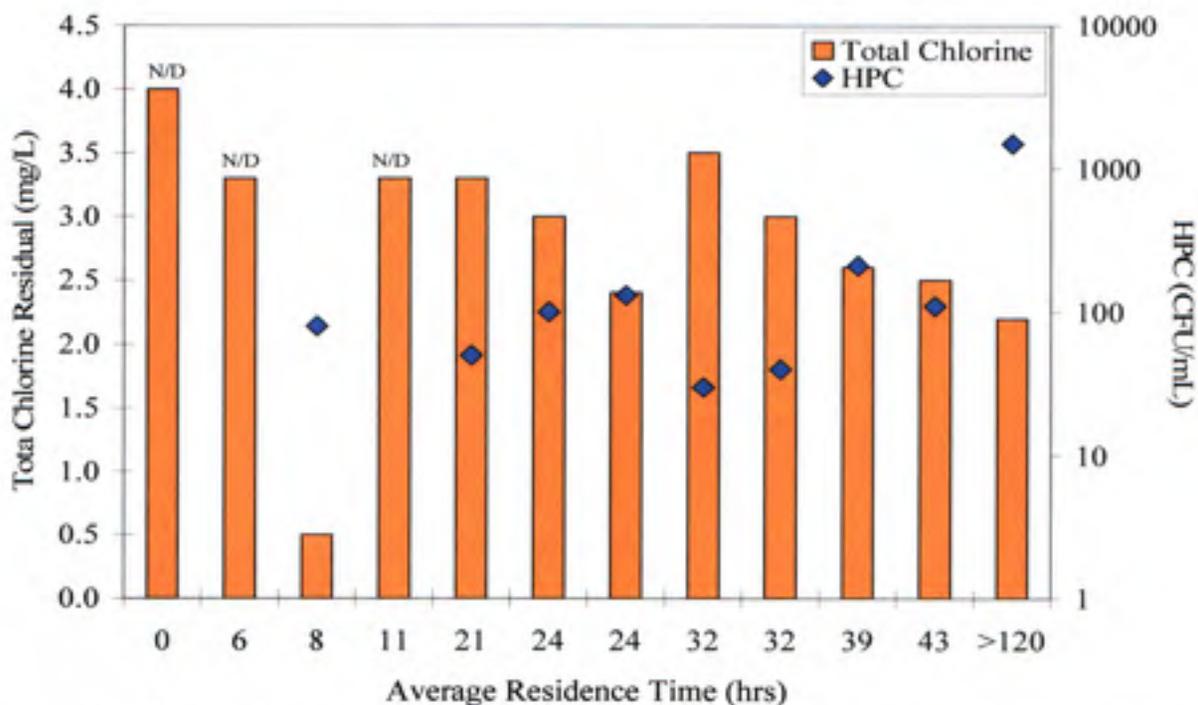


Figure A.2 Total chlorine residual and HPC versus average residence time for Utility C for 10/15/02

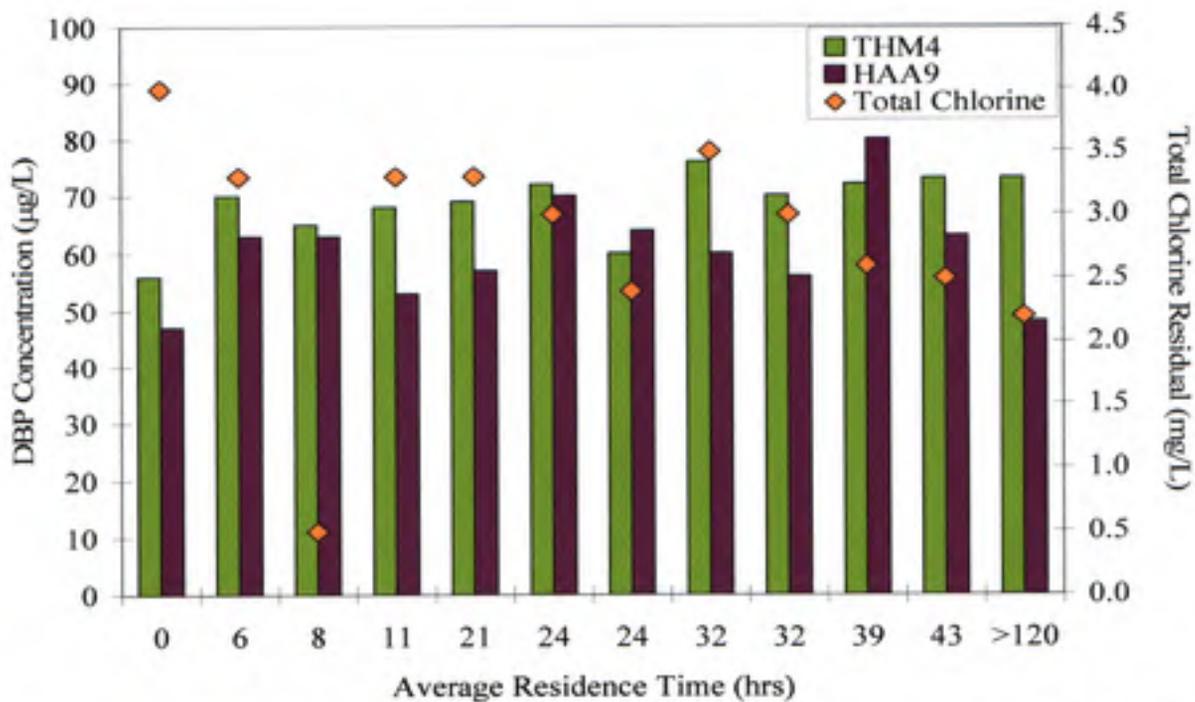


Figure A.3 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 10/15/02

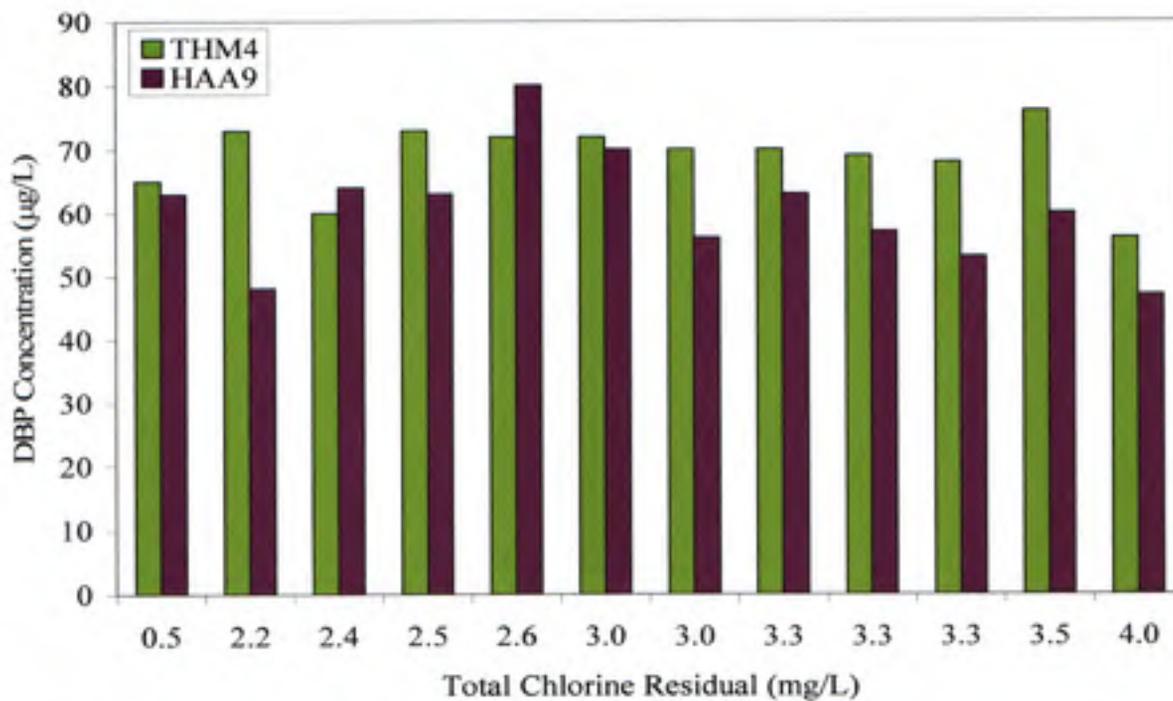


Figure A.4 THM4 and HAA9 versus total chlorine residual for Utility C for 10/15/02

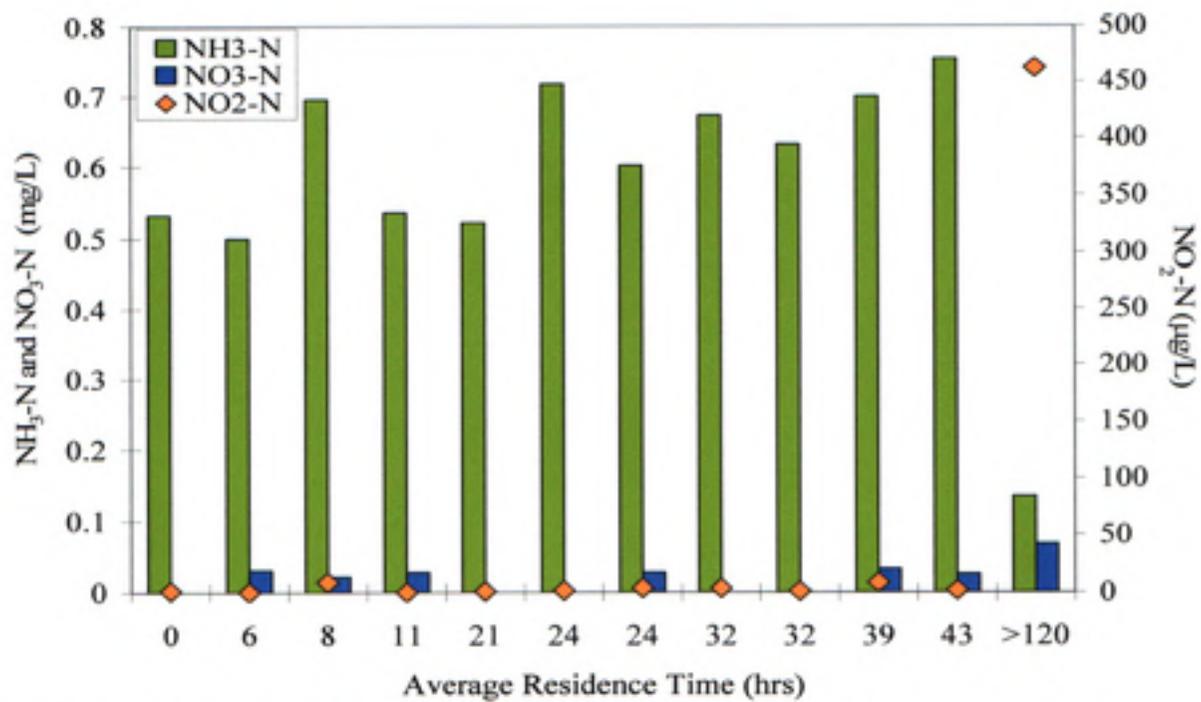


Figure A.5 Nitrogen species versus average residence time for Utility C for 10/15/02

Table A.5

pH, temperature and chlorine data for Utility C for 11/18/02

Sample ID	Temperature (°C)	pH	Total Cl <sub>2</sub> (mg/L)
POE	16	7.4	4.0
1	15	7.6	4.2
2	16	7.8	3.4
3	17	8.1	3.5
4	16	7.1	3.6
8	16	7.0	3.9
9	16	6.9	3.9
10	15	7.0	3.9
13	15	6.6	3.8
20	17	7.4	2.6
15	17	6.9	0.01
1721	17	7.4	3.1

Table A.6

Organic carbon, microbiological and nitrogen data for Utility C for 11/18/02

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE	262	2.53	0.049	0.0E+00	0.559	0.56	<0.020
1		2.47	0.045	6.5E+01	0.535	0.66	0.033
2		2.40	0.049	4.0E+01	0.554	1.25	0.042
3		2.57	0.048	4.5E+01	0.555	1.45	0.025
4		2.49	0.049	1.4E+02	0.569	0.86	0.033
8		2.42	0.044	7.0E+01	0.559	0.92	<0.020
9		2.55	0.049	1.2E+02	0.552	0.69	0.041
10		2.69	0.044	1.3E+02	0.559	0.69	0.033
13		2.81	0.032	8.0E+01	0.563	0.76	0.026
20		2.51	0.04	1.5E+02	0.581	3.65	0.051
15		2.12	0.028	2.6E+03	0.014	470	0.628
1721		2.52	0.045	7.0E+01	0.564	5.69	0.034

Table A.7

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility C for 11/18/02

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
POE	10	15	15	3	43
1	10	16	17	3	46
2	10	19	18	5	52
3	10	18	19	5	52
4	10	17	19	5	51
8	9	15	17	3	44
9	9	15	17	2	43
10	8	13	15	3	39
13	9	15	16	3	43
20	9	18	20	4	51
15	7	15	21	9	52
1721	9	15	18	4	46

Table A.8

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility C for 11/18/02

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
POE	4	20	8	15	8	7	13	5	2	82
1	3	17	7	12	7	5	10	4	<1	65
2	2	16	7	12	6	5	8	4	<1	60
3	3	16	7	11	6	5	9	4	<1	61
4	3	22	9	17	10	7	15	6	2	91
8	3	17	7	11	6	5	10	4	<1	63
9	3	18	7	13	6	5	10	4	<1	66
10	3	19	8	14	8	6	12	5	2	77
13	<2	22	10	19	10	8	16	6	2	93
20	3	19	8	14	8	5	9	4	2	72
15	3	16	6	12	10	5	10	7	4	73
1721	3	19	9	14	7	6	11	4	2	75

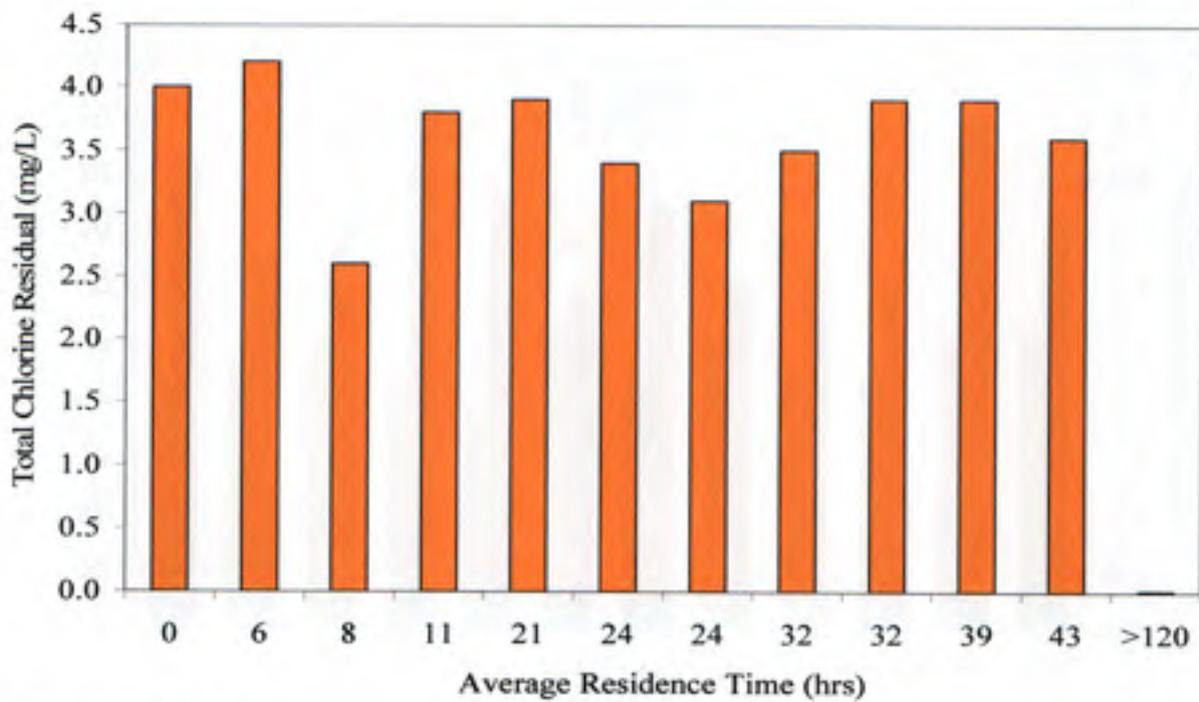


Figure A.6 Total chlorine residual versus average residence time for Utility C for 11/18/02

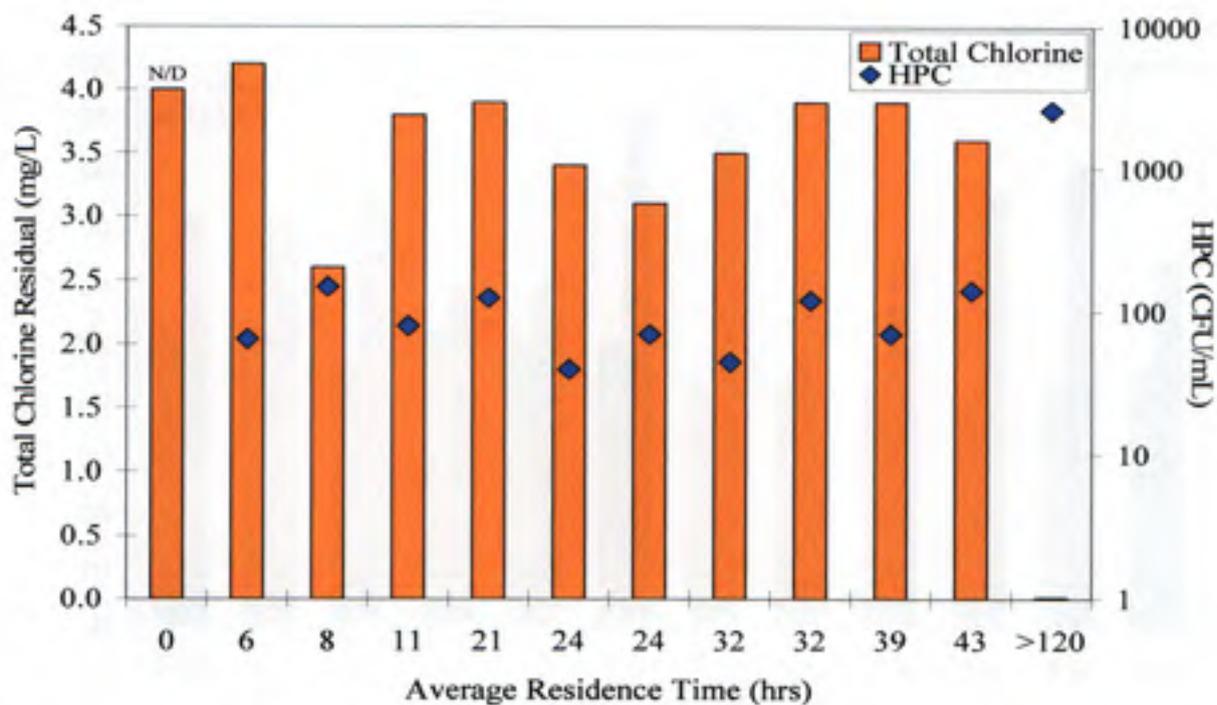


Figure A.7 Total chlorine residual and HPC versus average residence time for Utility C for 11/18/02

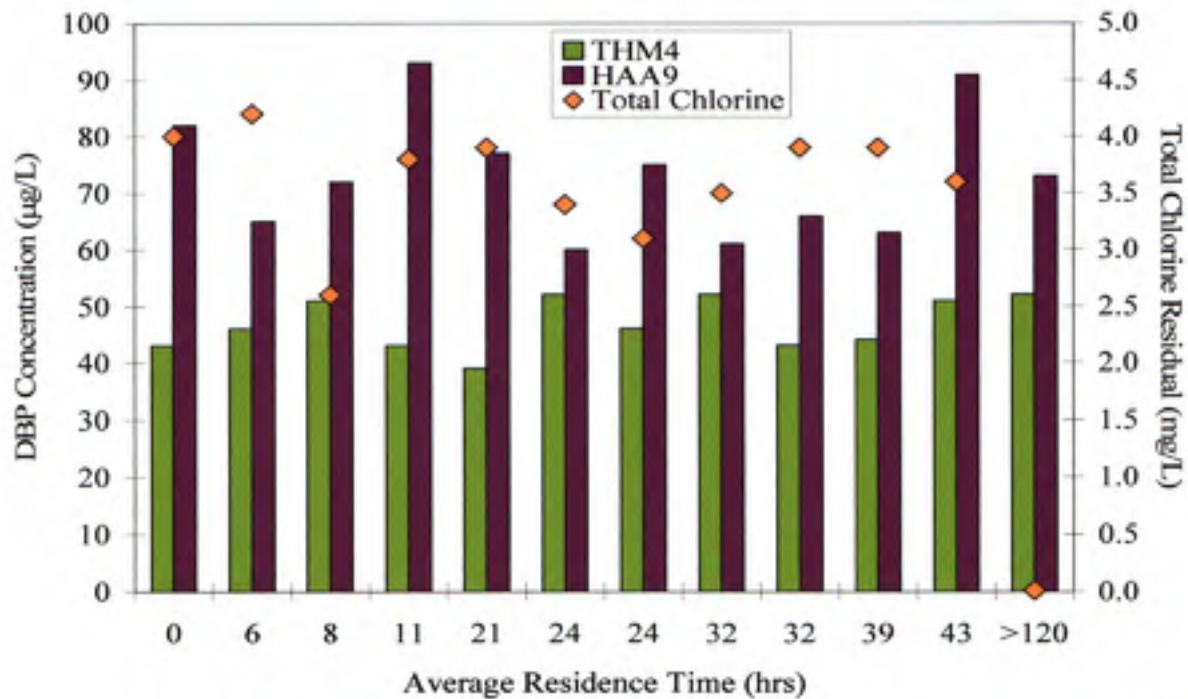


Figure A.8 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 11/18/02

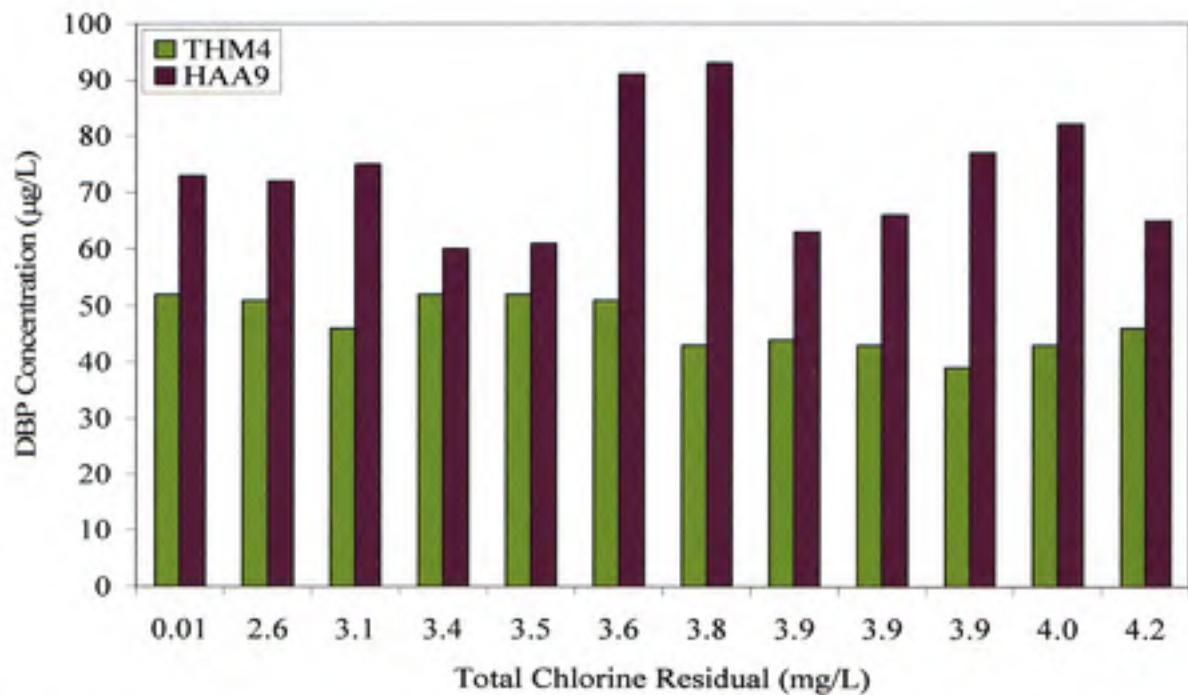


Figure A.9 THM4 and HAA9 versus total chlorine residual for Utility C for 11/18/02

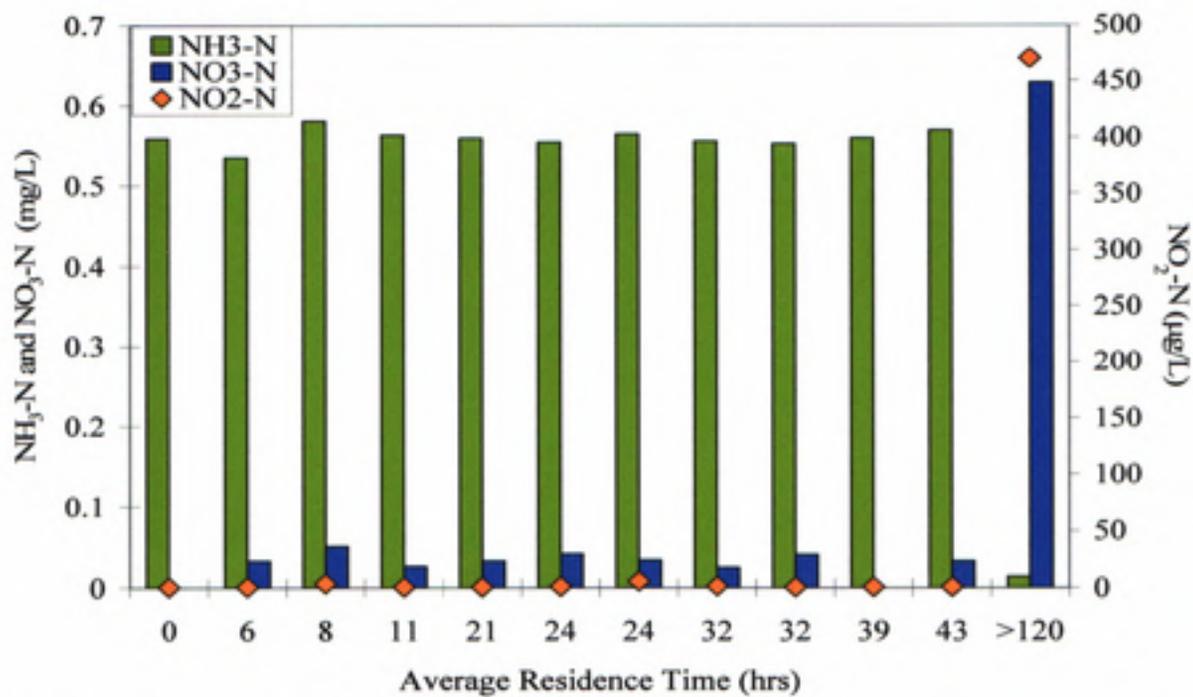


Figure A.10 Nitrogen species versus average residence time for Utility C for 11/18/02

Table A.9

pH, temperature and chlorine data for Utility C for 1/07/03

Sample ID	Temperature (°C)	pH	Total Cl <sub>2</sub> (mg/L)
POE	10.5	7.3	3.7
1	9.0	8.5	3.4
2	10.0	7.2	2.9
3	10.0	7.4	3.0
4	9.0	8.4	1.9
8	9.0	8.1	2.2
9	9.0	8.5	2.4
10	9.0	8.2	2.3
13	9.0	8.0	2.6
20	9.0	8.0	2.6
15	9.0	8.7	0.0
1721	10.0	8.0	2.8

Table A.10

Organic carbon, microbiological and nitrogen data for Utility C for 1/07/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE	293	3.17	0.05	0.0E+00	0.466	1.32	0.041
1		3.00	0.05	0.0E+00	0.462	0.62	0.056
2		3.15	0.05	1.5E+02	0.519	1.18	0.077
3		2.90	0.05	2.0E+01	0.505	1.74	<0.020
4		3.35	0.05	1.0E+01	0.499	2.96	0.08
8		2.97	0.05	3.0E+01	0.493	3.06	0.053
9		2.98	0.05	1.2E+02	0.487	1.64	<0.020
10		3.04	0.04	1.5E+01	0.509	2.76	0.033
13		3.05	0.05	5.0E+00	0.507	2.63	0.047
20		3.14	0.05	4.0E+01	0.53	3.22	0.034
15		2.94	0.04	1.3E+03	0.022	391	0.577
1721		2.92	0.05	5.5E+01	0.503	4.19	0.063

Table A.11

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility C for 1/07/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
POE	34	12	3	<1	49
1	33	15	4	<1	52
2	36	15	4	<1	55
3	36	16	4	<1	56
4	36	17	4	<1	57
8	35	16	4	<1	55
9	37	16	4	<1	57
10	35	16	4	<1	55
13	37	16	4	<1	57
20	37	16	4	<1	57
15	33	14	3	<1	50
1721	34	16	4	<1	54

Table A.12

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility C for 1/07/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
POE	3	5	15	5	1	15	5	1	<1	50
1	<2	6	15	5	2	15	5	2	<1	50
2	3	6	19	6	2	18	6	2	<1	62
3	<2	7	21	6	2	17	6	2	<1	61
4	3	6	19	6	2	16	5	2	<1	59
8	3	6	18	6	1	16	5	2	<1	57
9	2	6	16	5	1	12	5	1	<1	48
10	3	5	14	5	2	12	5	1	<1	47
13	3	5	16	5	2	14	5	2	<1	52
20	4	5	15	5	2	12	5	1	<1	49
15	<2	3	7	2	<1	12	5	2	<1	31
1721	3	5	16	5	2	12	4	1	<1	48

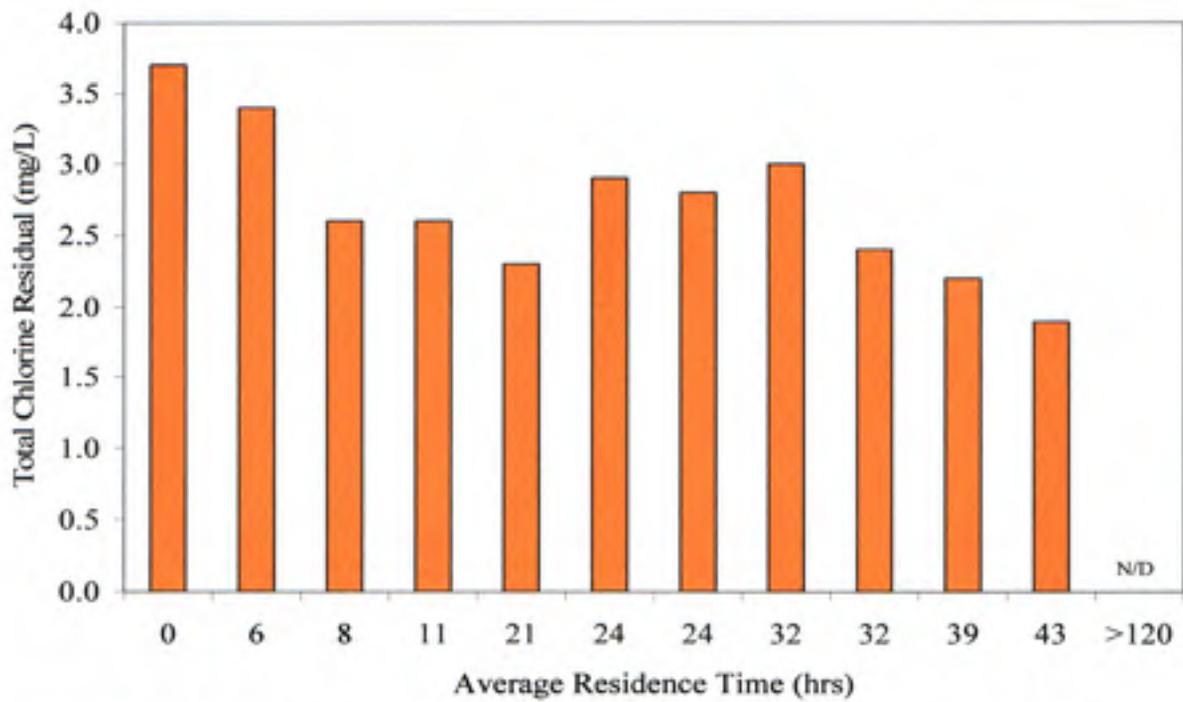


Figure A.11 Total chlorine residual versus average residence time for Utility C for 1/07/03

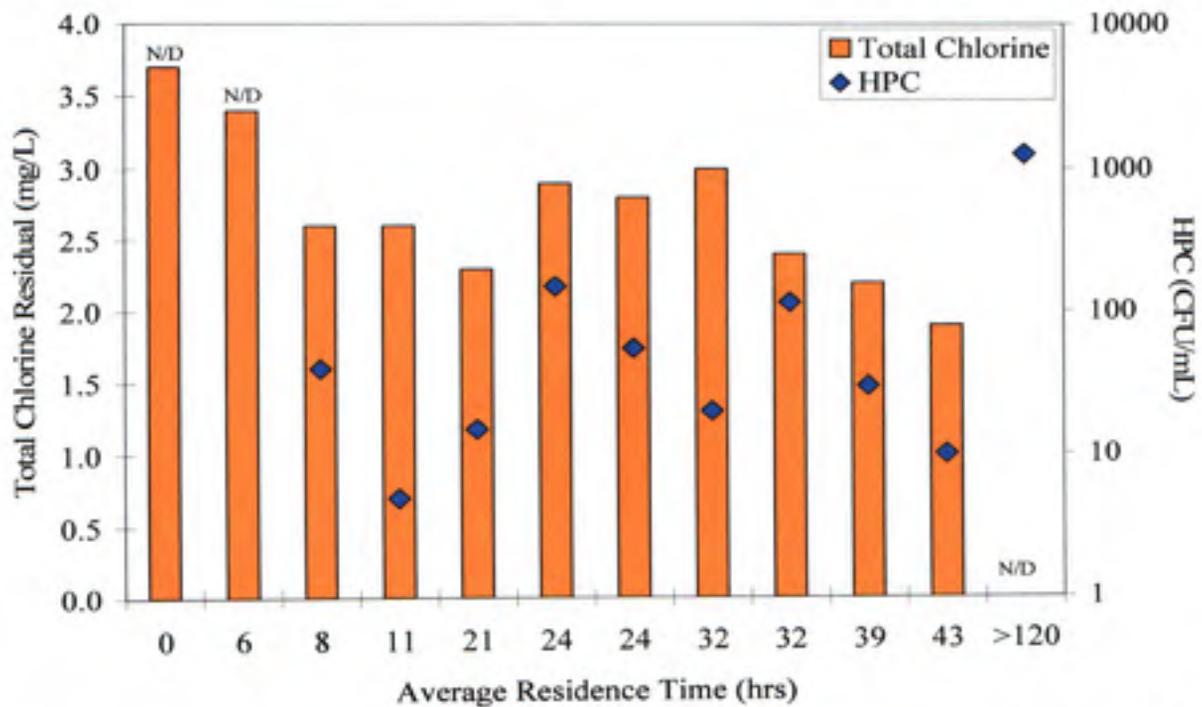


Figure A.12 Total chlorine residual and HPC versus average residence time for Utility C for 1/07/03

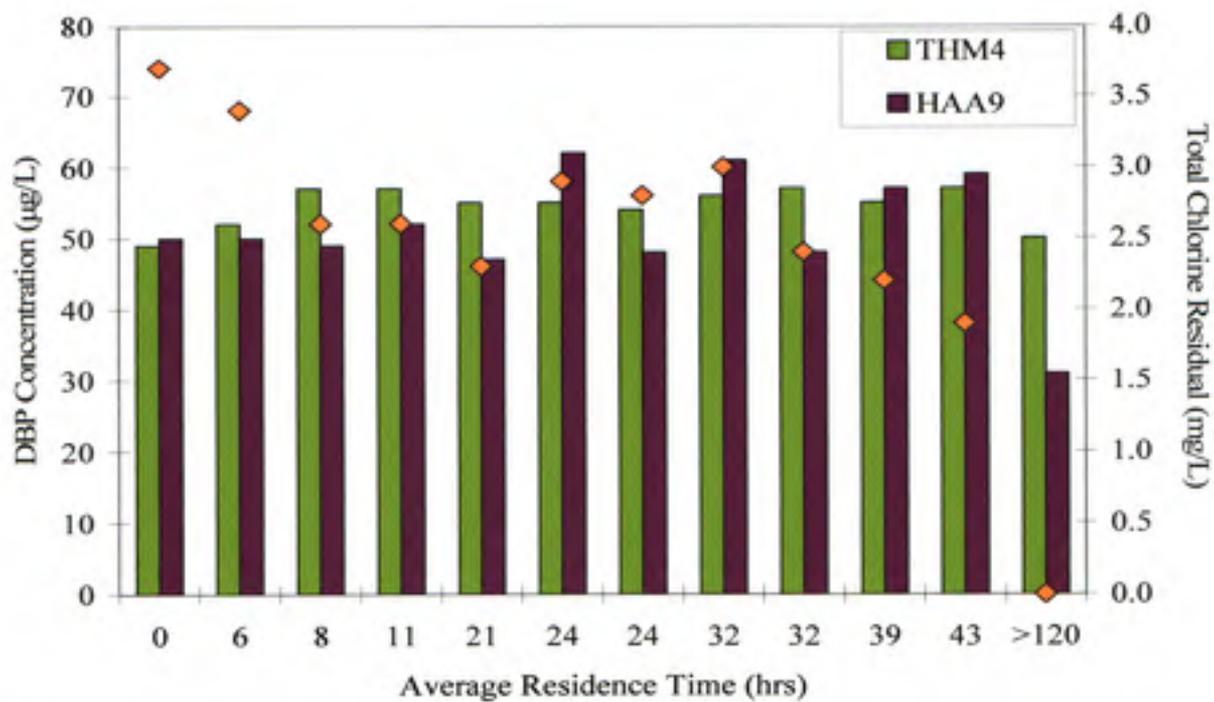


Figure A.13 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 1/07/03

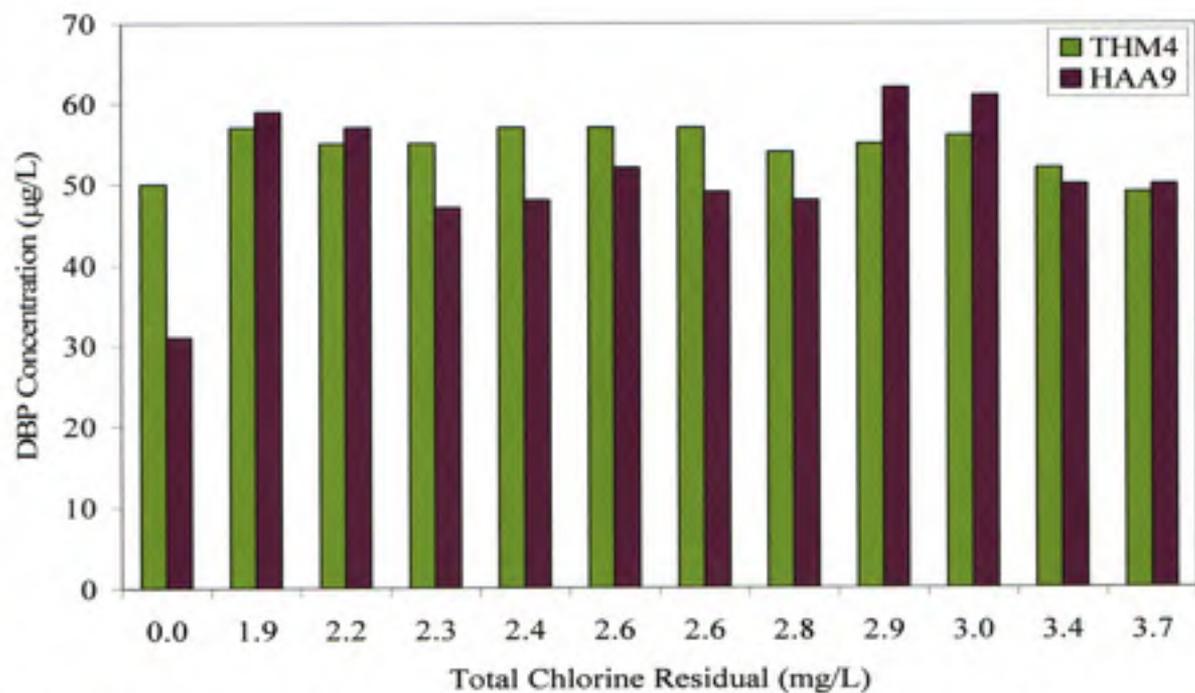


Figure A.14 THM4 and HAA9 versus total chlorine residual for Utility C for 1/07/03

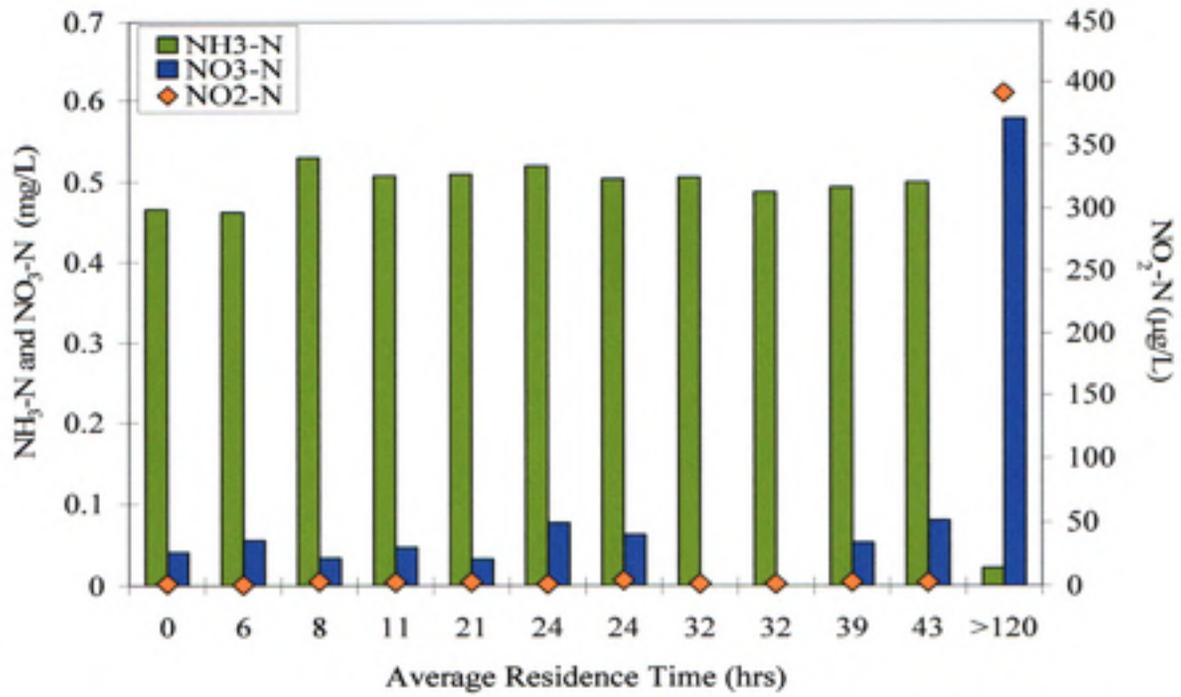


Figure A.15 Nitrogen species versus average residence time for Utility C for 1/07/03

Table A.13

pH, temperature and chlorine data for Utility C for 2/25/03

Sample ID	Temperature (°C)	pH	Total Cl <sub>2</sub> (mg/L)
POE	NA	NA	NA
1	8.0	7.7	3.3
2	8.0	7.7	2.9
3	8.0	8.0	3.1
4	8.0	8.1	2.5
8	8.0	8.1	3.0
9	8.0	8.0	2.5
10	8.0	8.1	3.0
13	8.0	8.2	3.0
20	9.0	8.3	1.4
15	7.0	8.1	2.0
1721	10.0	8.2	2.4

Table A.14

Organic carbon, microbiological and nitrogen data for Utility C for 2/25/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE	421	3.10	0.059	0.0E+00	0.426	4.08	0.030
1		3.08	0.055	0.0E+00	0.424	3.42	0.047
2		3.09	0.059	0.0E+00	0.457	4.95	0.053
3		3.07	0.06	0.0E+00	0.446	4.76	0.053
4		3.08	0.059	3.0E+00	0.438	5.67	0.068
8		3.05	0.058	1.0E+00	0.441	5.00	0.042
9		3.14	0.058	0.0E+00	0.422	4.56	0.057
10		3.03	0.060	0.0E+00	0.452	3.94	0.035
13		3.04	0.059	1.0E+00	0.461	4.33	0.044
20		3.04	0.059	3.0E+00	0.467	6.87	0.044
15		3.08	0.055	4.0E+01	0.425	14.4	0.091
1721		3.07	0.058	1.0E+00	0.442	9.47	0.057

Table A.15

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility C for 2/25/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
POE	34	12	3	<1	49
1	33	15	4	<1	52
2	36	15	4	<1	55
3	36	16	4	<1	56
4	36	17	4	<1	57
8	35	16	4	<1	55
9	37	16	4	<1	57
10	35	16	4	<1	55
13	37	16	4	<1	57
20	37	16	4	<1	57
15	33	14	3	<1	50
1721	51	12	2	<1	65

Table A.16

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility C for 2/25/03

Sample ID	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	HAA9
POE	3	4	21	4	1	19	4	<1	<1	56
1	<2	4	21	4	1	20	4	<1	<1	54
2	<2	5	24	5	1	23	5	1	<1	64
3	2	5	23	5	1	20	4	1	<1	61
4	2	5	25	5	1	22	5	<1	<1	65
8	4	5	25	5	1	23	5	1	<1	69
9	<2	6	28	6	2	26	5	1	<1	74
10	3	5	24	5	1	22	5	1	<1	66
13	2	4	21	4	1	19	4	<1	<1	55
20	3	5	25	5	2	23	5	<1	<1	68
15	2	5	26	5	1	21	4	<1	<1	64
1721	3	4	22	4	1	19	4	<1	<1	57

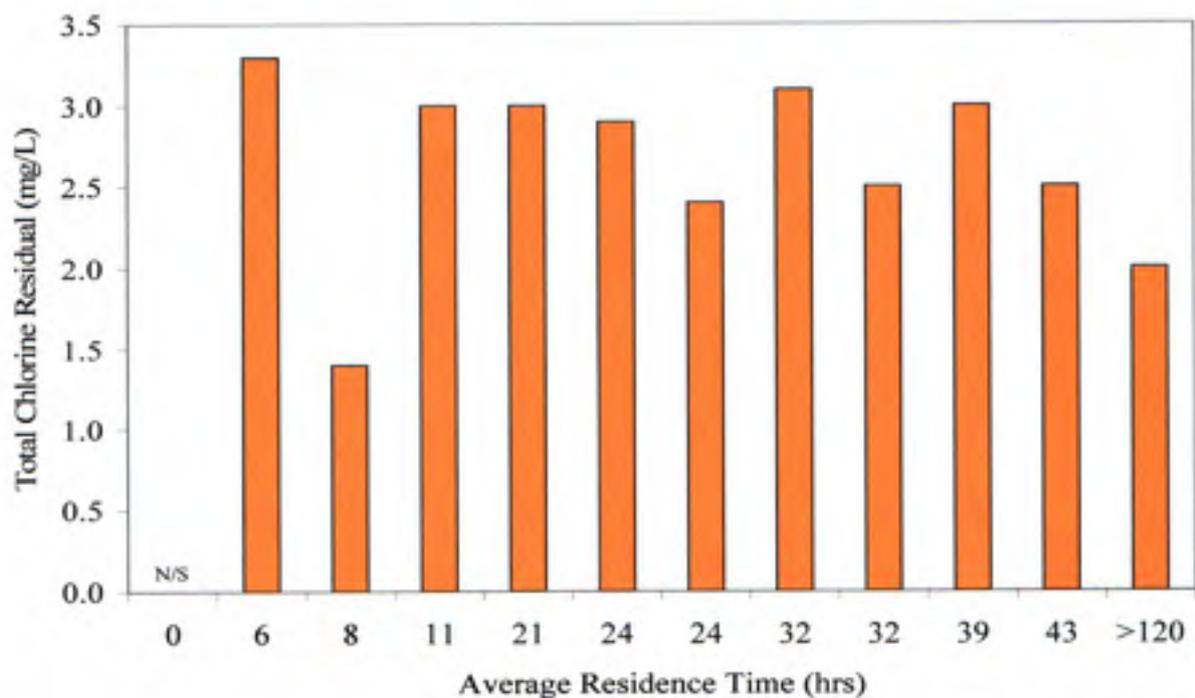


Figure A.16 Total chlorine residual versus average residence time for Utility C for 2/25/03

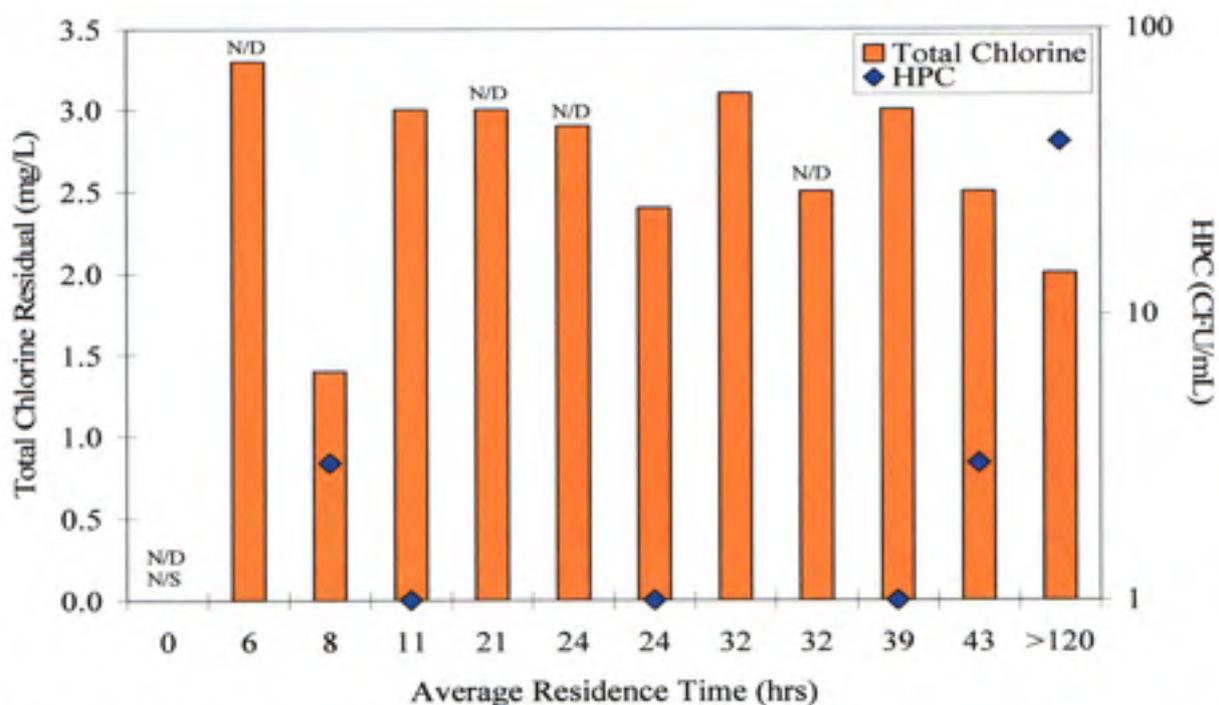


Figure A.17 Total chlorine residual and HPC versus average residence time for Utility C for 2/25/03

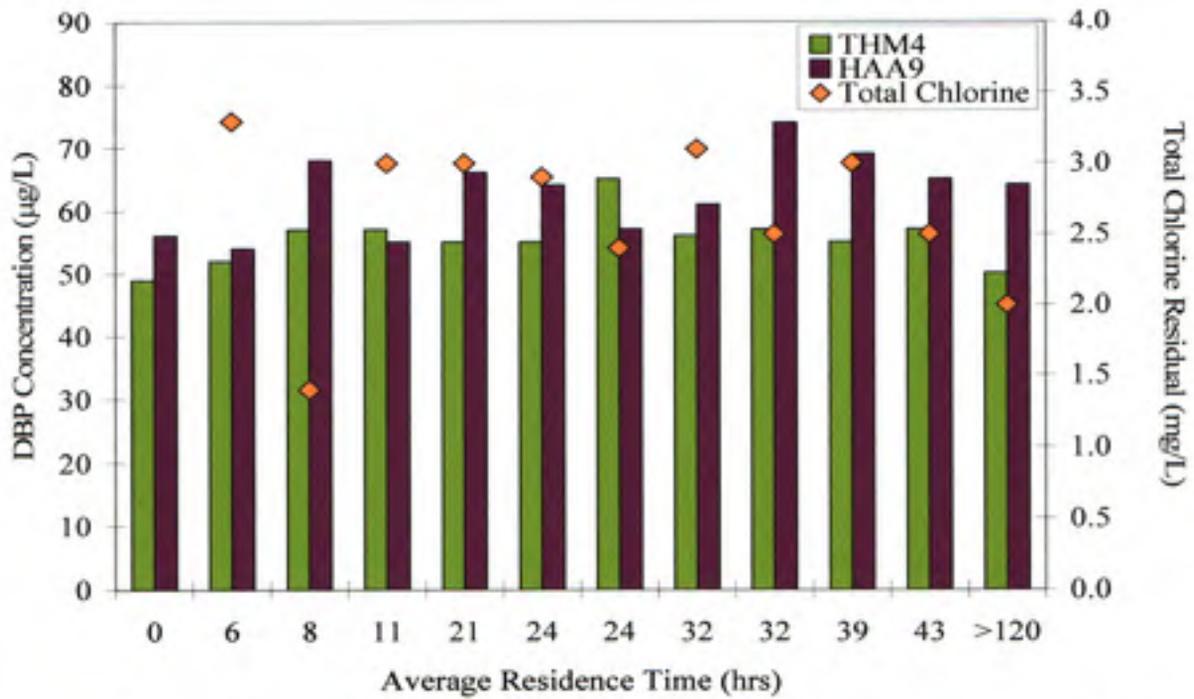


Figure A.18 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 2/25/03

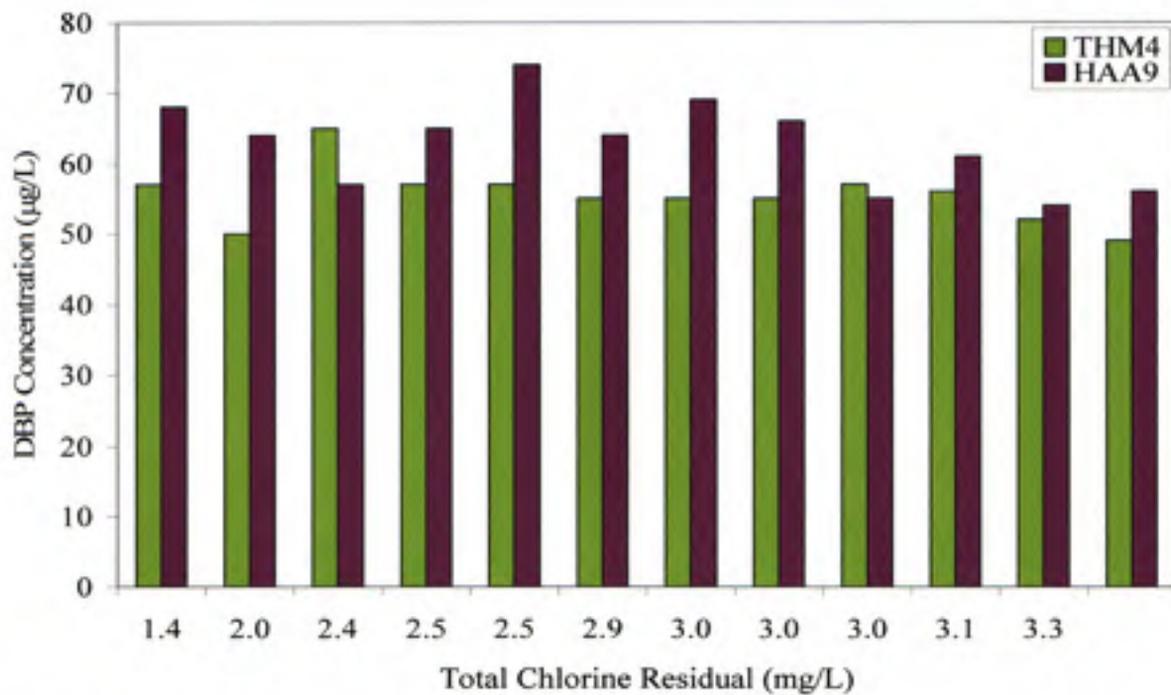


Figure A.19 THM4 and HAA9 versus total chlorine residual for Utility C for 2/25/03

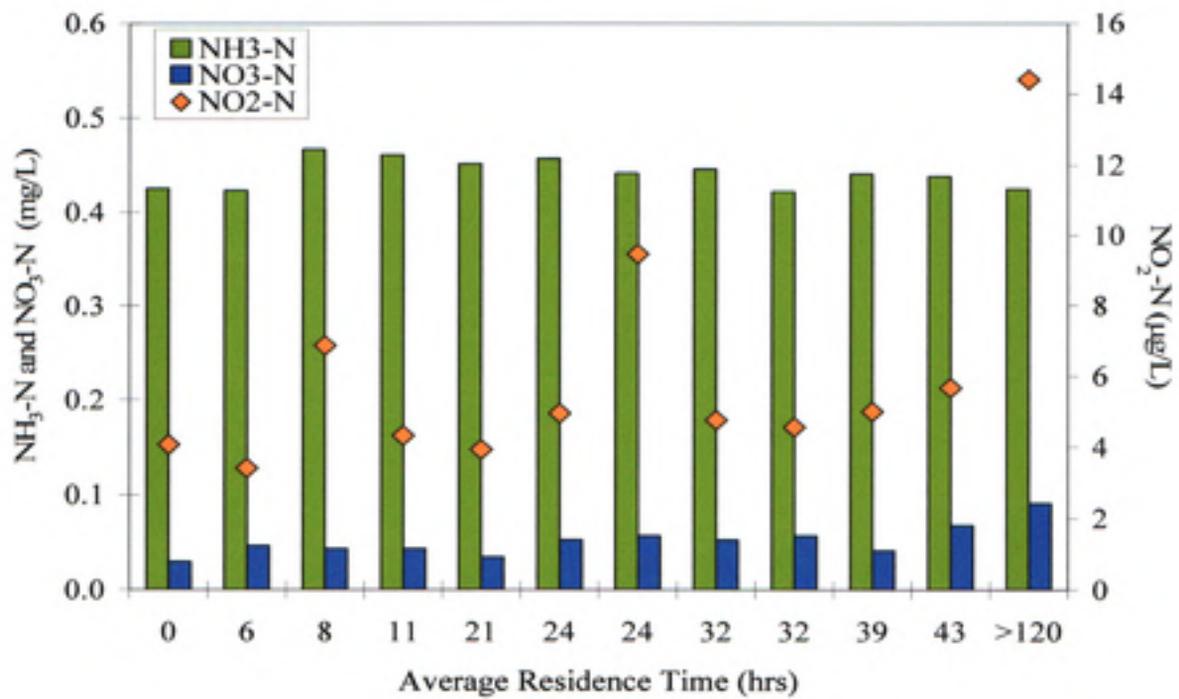


Figure A.20 Nitrogen species versus average residence time for Utility C for 2/25/03

Table A.17

pH, temperature and chlorine data for Utility C for 4/29/03

Sample ID	Temperature (°C)	pH	Total Cl <sub>2</sub> (mg/L)
POE	20	7.6	3.3
1	19	7.1	2.6
2	18	7.0	2.5
3	17	7.2	2.4
4	19	7.1	2.4
8	18	7.0	2.5
9	18	6.9	2.6
10	19	7.0	2.3
13	18	7.1	2.3
20	19	7.2	1.7
15	18	7.0	0.2
1721	19	7.3	1.9

Table A.18

Organic carbon, microbiological and nitrogen data for Utility C for 4/29/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE	224	2.97	0.050	0.0E+00	0.474	1.05	0.035
1		3.08	0.048	0.0E+00	0.482	1.46	0.042
2		3.09	0.054	1.6E+01	0.498	1.18	0.061
3		3.21	0.055	1.0E+00	0.441	4.35	0.045
4		3.07	0.054	8.0E+00	0.455	1.38	0.034
8		3.18	0.054	1.6E+01	0.48	1.78	0.045
9		3.09	0.05	4.0E+00	0.487	1.68	0.039
10		3.05	0.054	2.2E+01	0.513	1.26	0.046
13		3.05	0.054	5.0E+00	0.516	0.73	0.051
20		3.10	0.052	2.0E+01	0.500	4.74	0.060
15		2.88	0.041	1.2E+04	0.060	817.9	0.446
1721		3.03	0.052	1.6E+01	0.494	11.87	0.056

Table A.19

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility C for 4/29/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
POE	58	12	2	<1	72
1	57	13	2	<1	72
2	64	13	2	<1	79
3	76	15	2	<1	93
4	62	14	2	<1	78
8	60	13	2	<1	75
9	61	14	1	<1	76
10	65	13	2	<1	80
13	64	13	2	<1	79
20	66	14	2	<1	82
15	63	13	2	<1	78
1721	66	13	2	<1	81

Table A.20

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility C for 4/29/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
POE	3	4	33	4	2	32	5	1	<1	84
1	3	3	31	4	1	31	4	<1	<1	77
2	<2	4	33	4	1	32	4	<1	<1	78
3	3	4	33	4	1	31	4	<1	<1	80
4	<2	3	28	3	1	27	4	<1	<1	66
8	5	3	31	4	1	31	4	<1	<1	79
9	<2	3	28	4	<1	28	3	<1	<1	66
10	3	3	31	4	1	30	4	<1	<1	76
13	<2	3	32	4	1	30	4	<1	<1	74
20	<2	3	31	4	1	30	4	<1	<1	73
15	<2	2	20	3	<1	27	4	1	<1	57
1721*	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

\* No data available. The extract was white, cloudy in appearance, and the duplicate was used as a spike sample, so no sample was available.

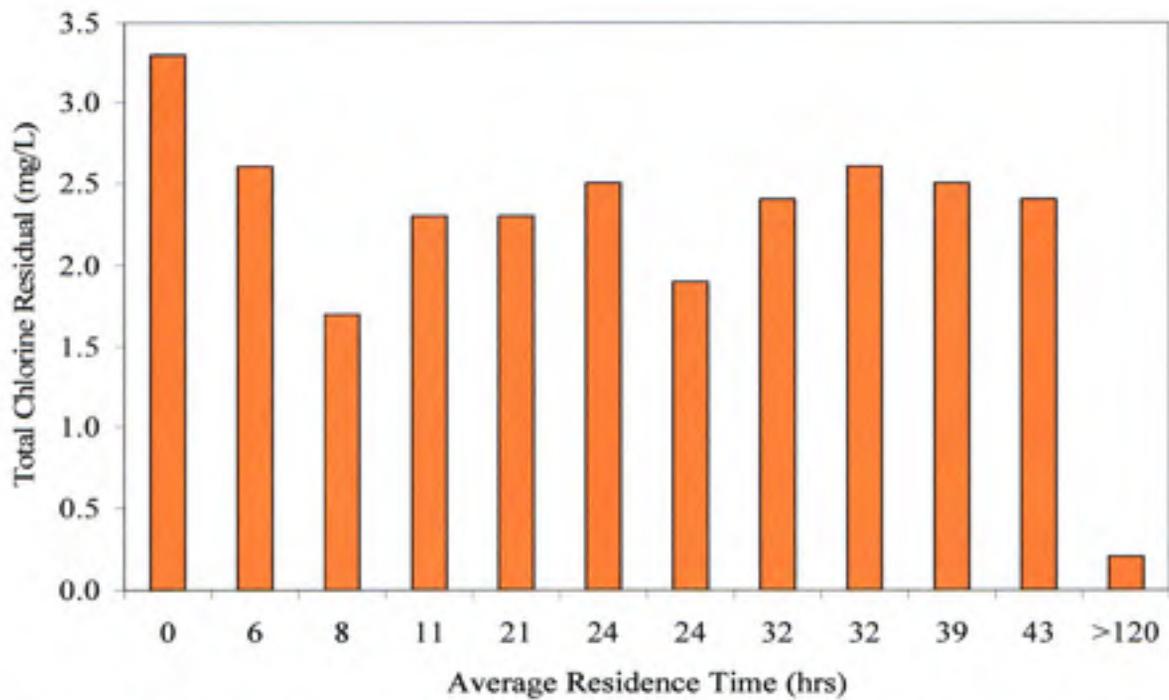


Figure A.21 Total chlorine residual versus average residence time for Utility C for 4/29/03

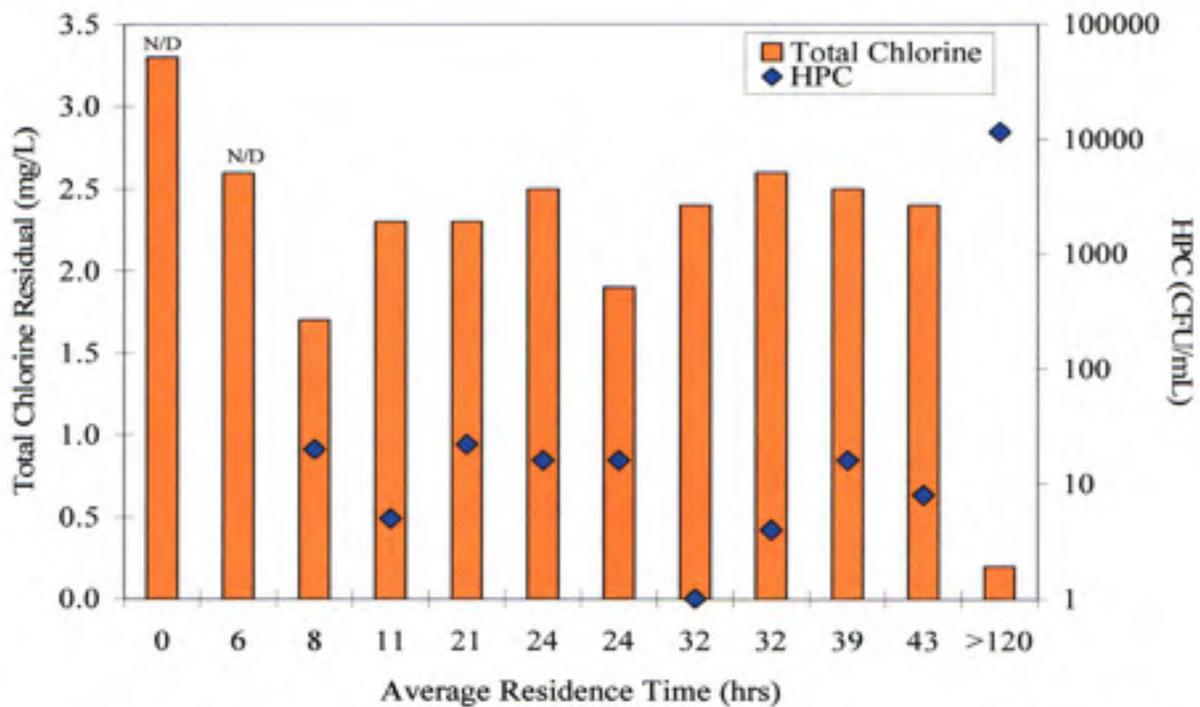


Figure A.22 Total chlorine residual and HPC versus average residence time for Utility C for 4/29/03

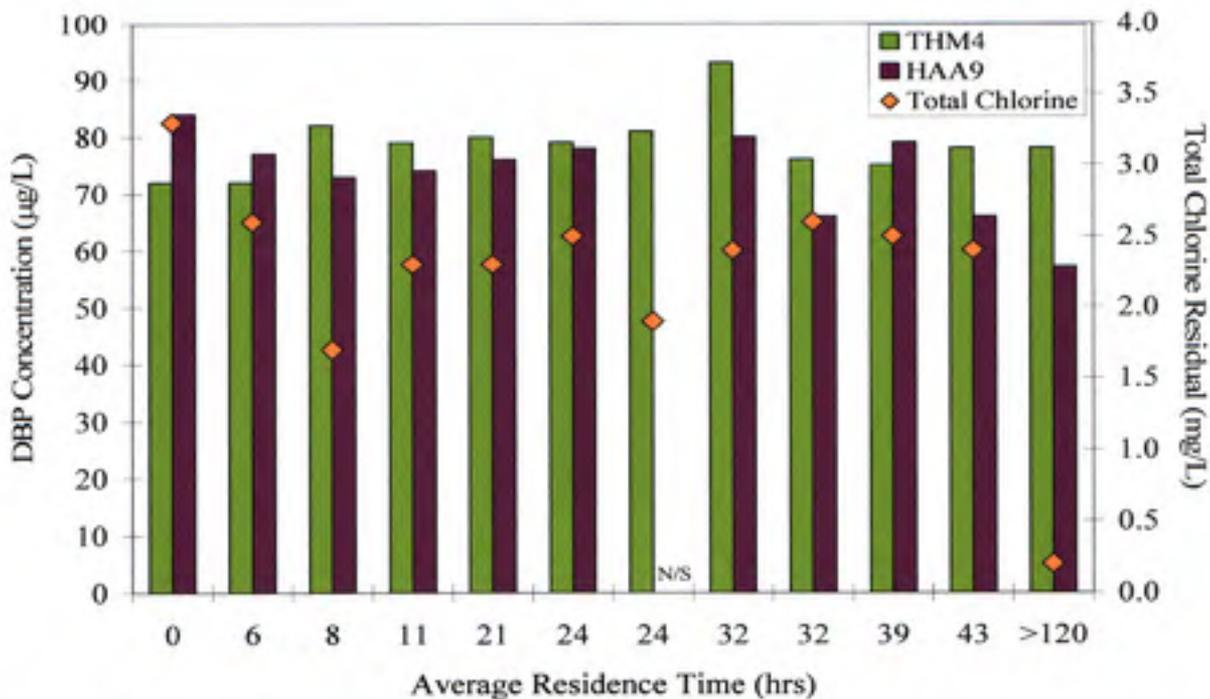


Figure A.23 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 4/29/03

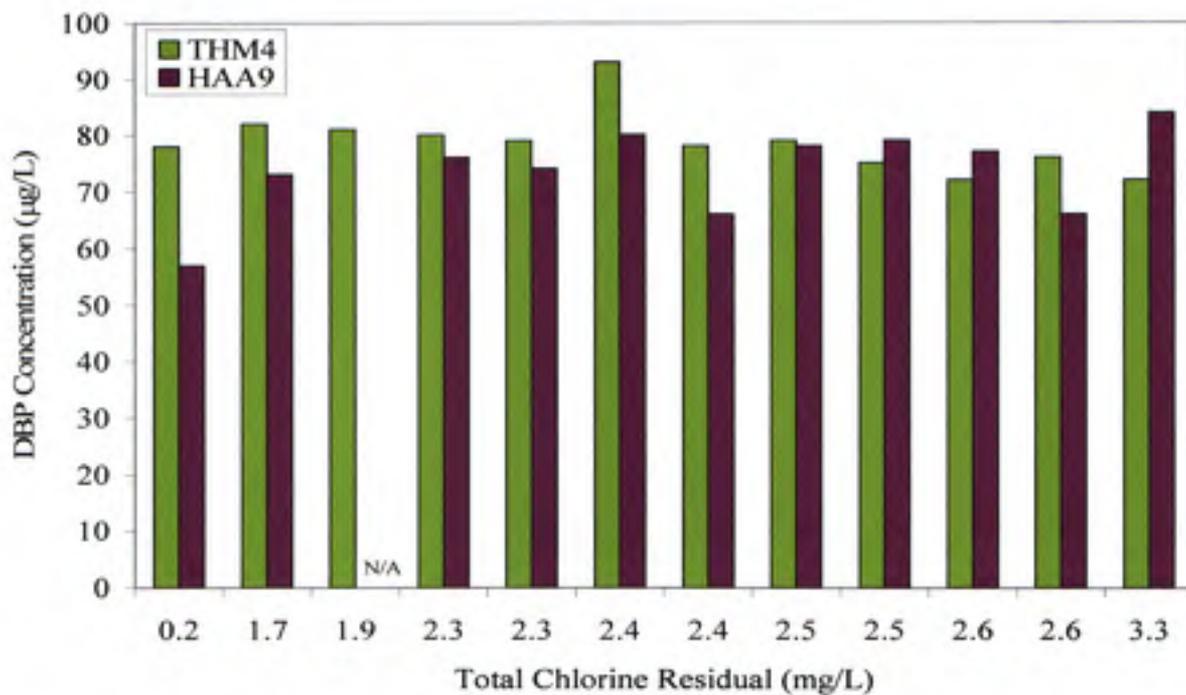


Figure A.24 THM4 and HAA9 versus total chlorine residual for Utility C for 4/29/03

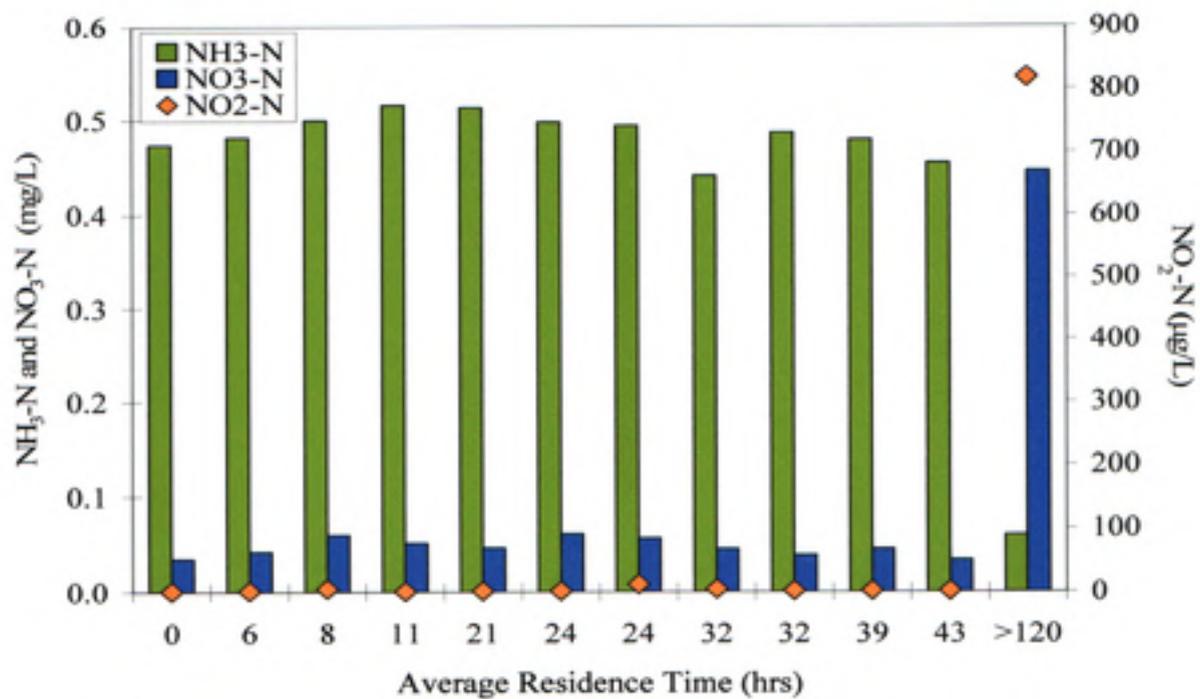


Figure A.25 Nitrogen species versus average residence time for Utility C for 4/29/03

Table A.21

pH, temperature and chlorine data for Utility C for 6/11/03

Sample ID	Temperature (°C)	pH	Total Cl <sub>2</sub> (mg/L)
POE	25	7.4	3.9
1	24	7.2	3.5
2	22	7.1	2.2
3	23	7.1	2.9
4	23	7.1	2.2
8	24	7.1	3.2
9	23	7.1	3.2
10	24	7.2	2.6
13	24	7.1	3.0
20	23	7.1	1.8
15	22	7.0	0.3
1721	24	7.1	2.4

Table A.22

Organic carbon, microbiological and nitrogen data for Utility C for 6/11/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE	307*	3.07	0.062	ND	0.543	0.62	<0.020
1		3.05	0.056	1	0.503	<0.50	0.022
2		2.97	0.058	22	0.599	1.2	<0.020
3		3.000	0.060	6	0.551	0.57	0.02
4		2.93	0.058	32	0.598	1.04	0.039
8		3.11	0.063	4	0.545	0.84	<0.020
9		3.04	0.062	6	0.558	<0.50	0.033
10		3.05	0.062	7	0.537	1.11	<0.020
13		3.04	0.064	4	0.526	<0.50	0.037
20		2.97	0.056	30	0.632	3.74	0.057
15		2.86	0.050	3400	0.137	412.1	0.341
1721		3.02	0.060	18	0.565	1.47	0.025

\* Collected on June 23, 2003

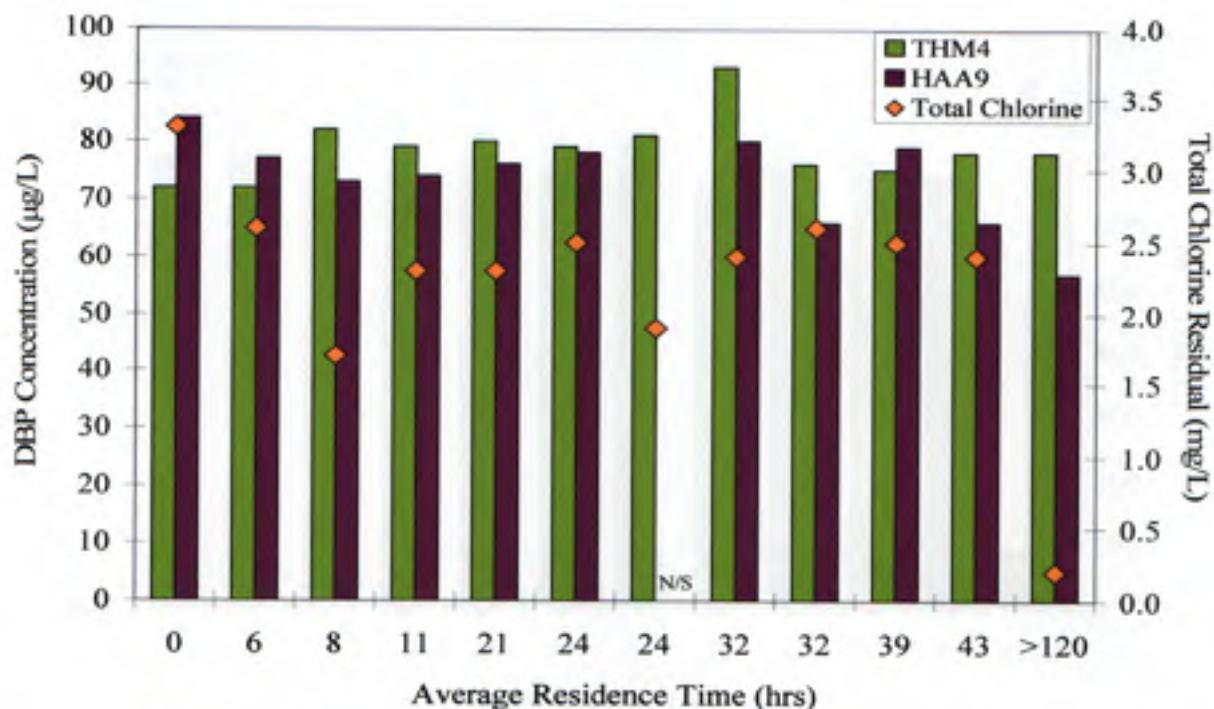


Figure A.23 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 4/29/03

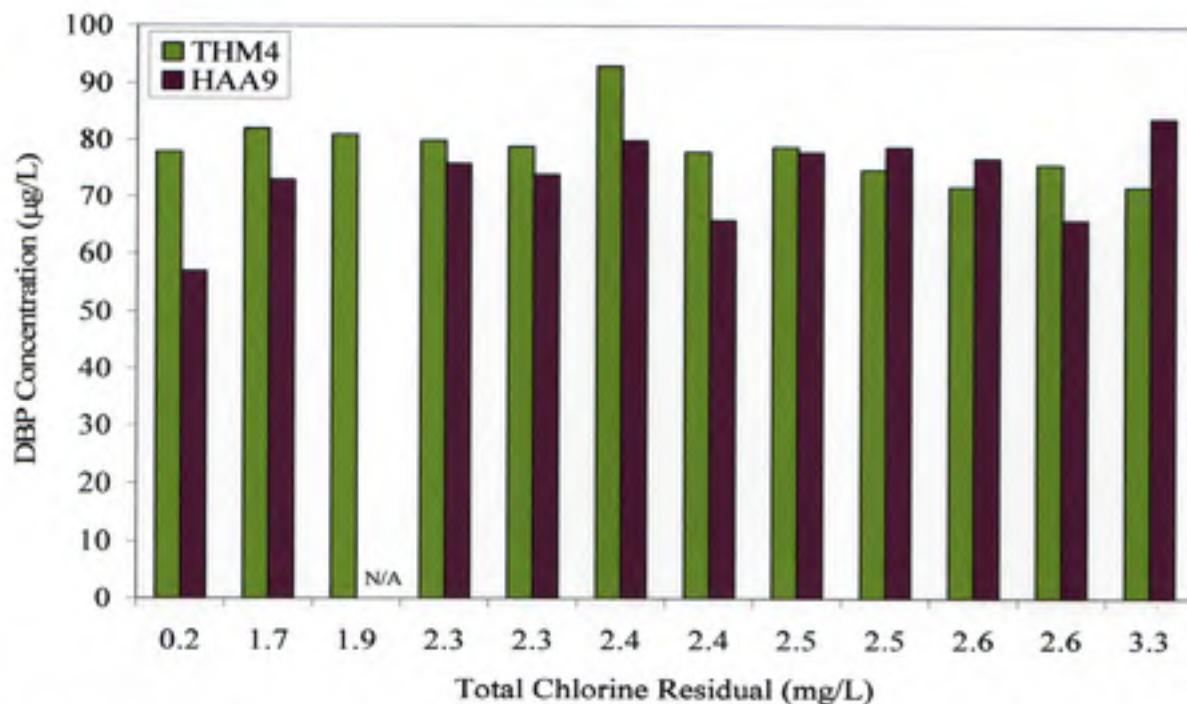


Figure A.24 THM4 and HAA9 versus total chlorine residual for Utility C for 4/29/03

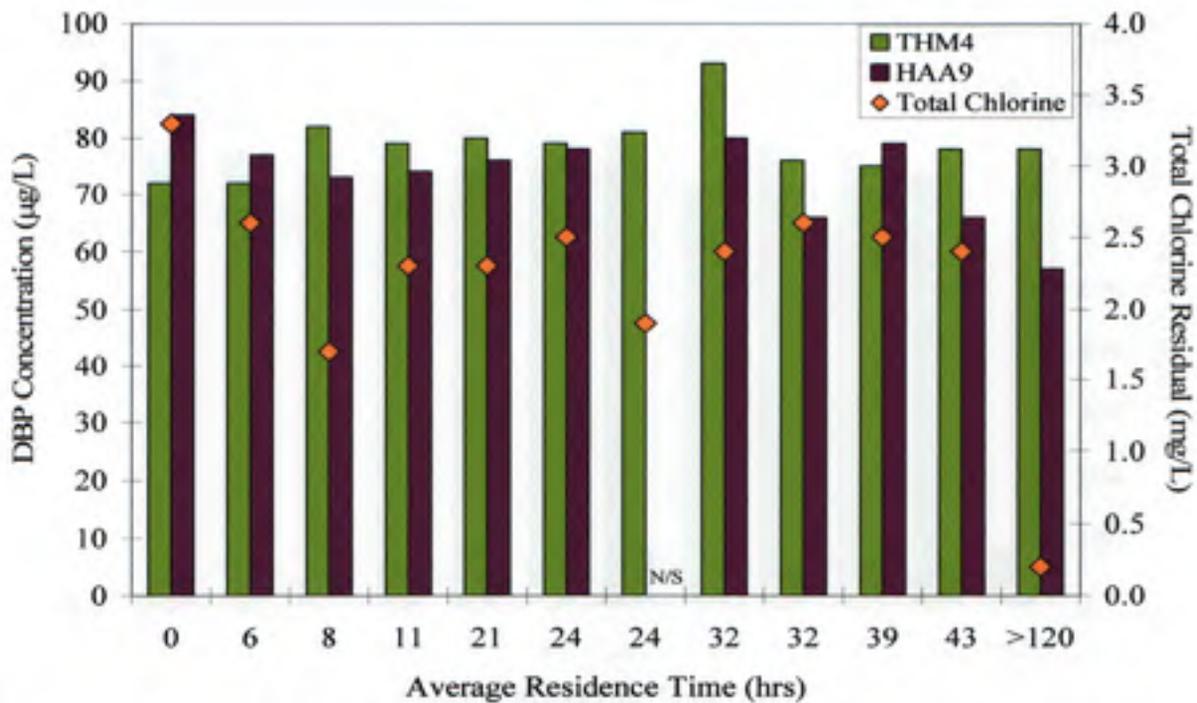


Figure A.23 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 4/29/03

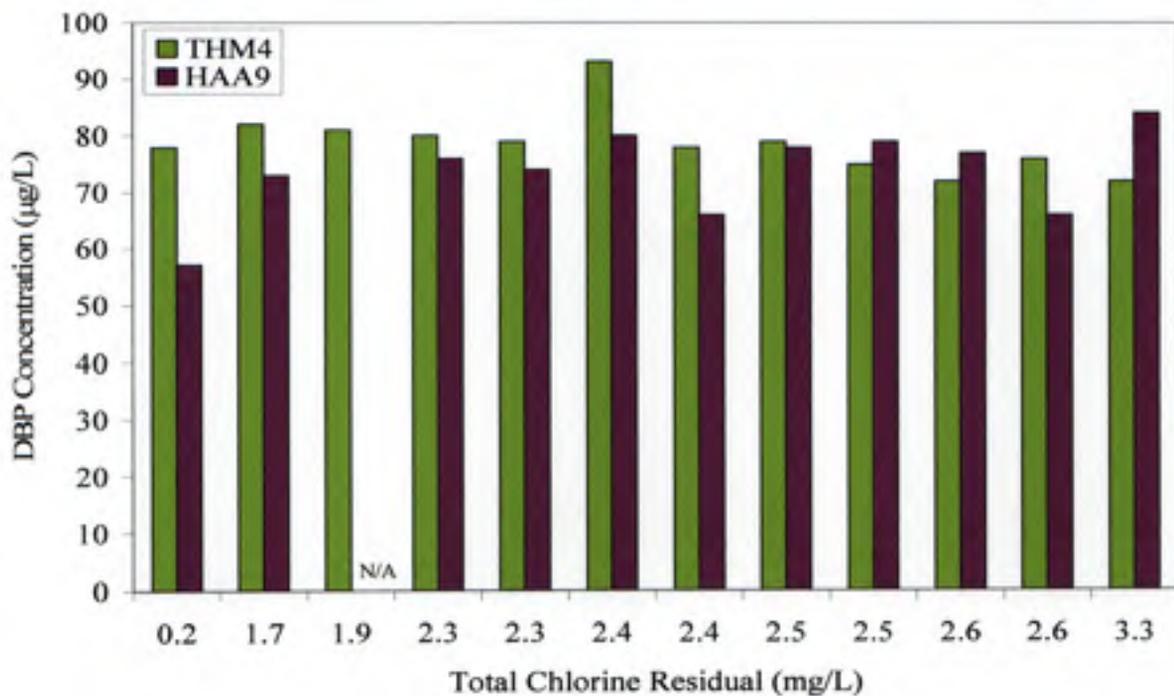


Figure A.24 THM4 and HAA9 versus total chlorine residual for Utility C for 4/29/03

Table A.23

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility C for 6/11/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
POE	62	11	2	<1	75
1	69	13	2	<1	84
2	69	14	2	<1	85
3	66	14	2	<1	82
4	65	14	2	<1	81
8	66	13	2	<1	81
9	63	13	2	<1	78
10	69	13	2	<1	84
13	67	13	2	<1	82
20	61	13	2	<1	76
15	55	11	1	<1	67
1721	62	13	2	<1	77

Table A.24

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility C for 6/11/03

Sample ID	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	HAA9
POE	NA	NA	NA	NA	NA	NA	NA	1	<1	1
1	<2	4	27	4	1	27	4	<1	<1	67
2	<2	4	29	4	1	27	4	<1	<1	69
3	<2	4	29	4	<1	26	3	<1	<1	66
4	<2	5	34	4	2	30	5	1	<1	81
8	<2	4	28	4	<1	27	4	<1	<1	67
9	<2	4	34	4	2	31	5	1	<1	81
10	<2	4	30	4	2	28	5	<1	<1	73
13	<2	3	26	3	2	25	4	<1	<1	63
20	<2	4	31	<1	2	28	4	<1	<1	69
15	<2	3	19	3	<1	21	3	1	<1	50
1721	<2	4	30	4	2	29	4	1	<1	74

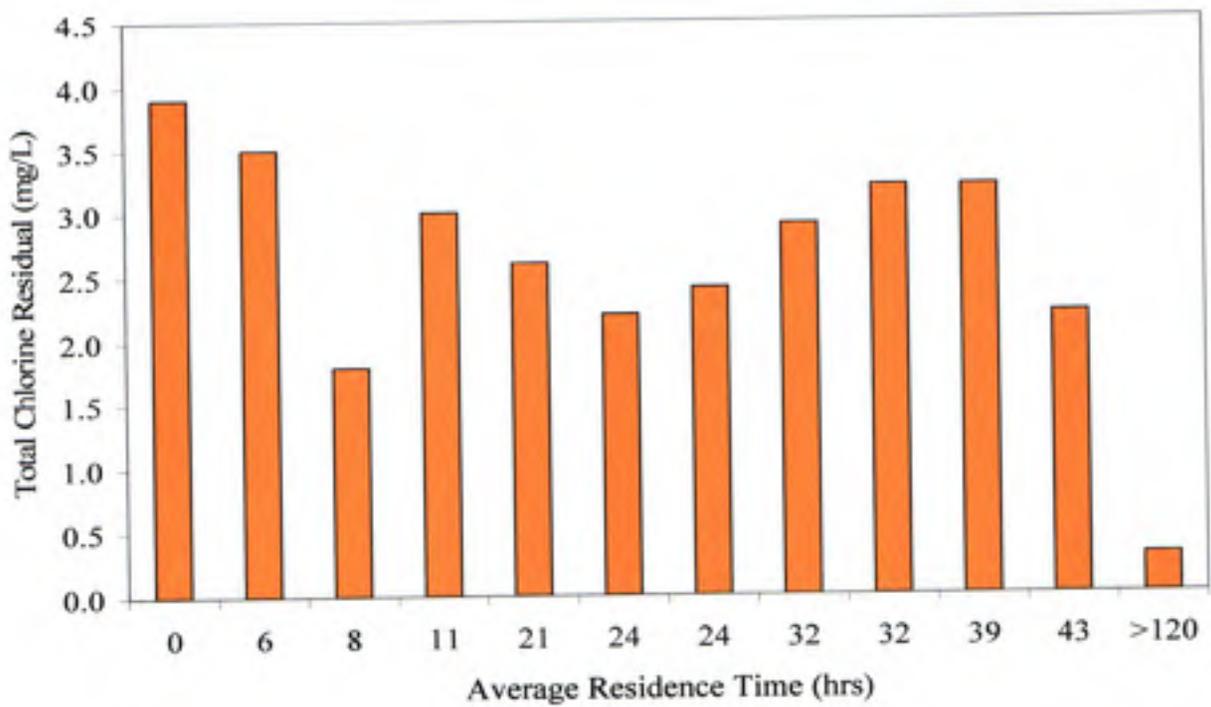


Figure A.26 Total chlorine residual versus average residence time for Utility C for 6/11/03

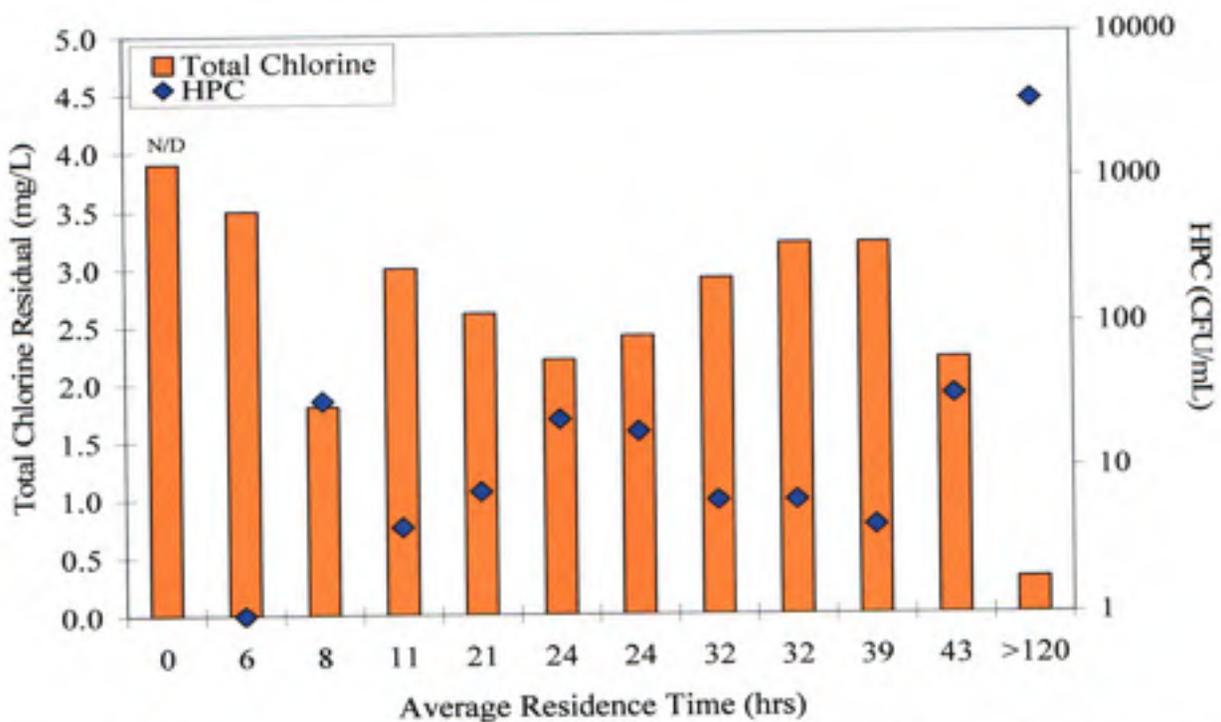


Figure A.27 Total chlorine residual and HPC versus average residence time for Utility C for 6/11/03

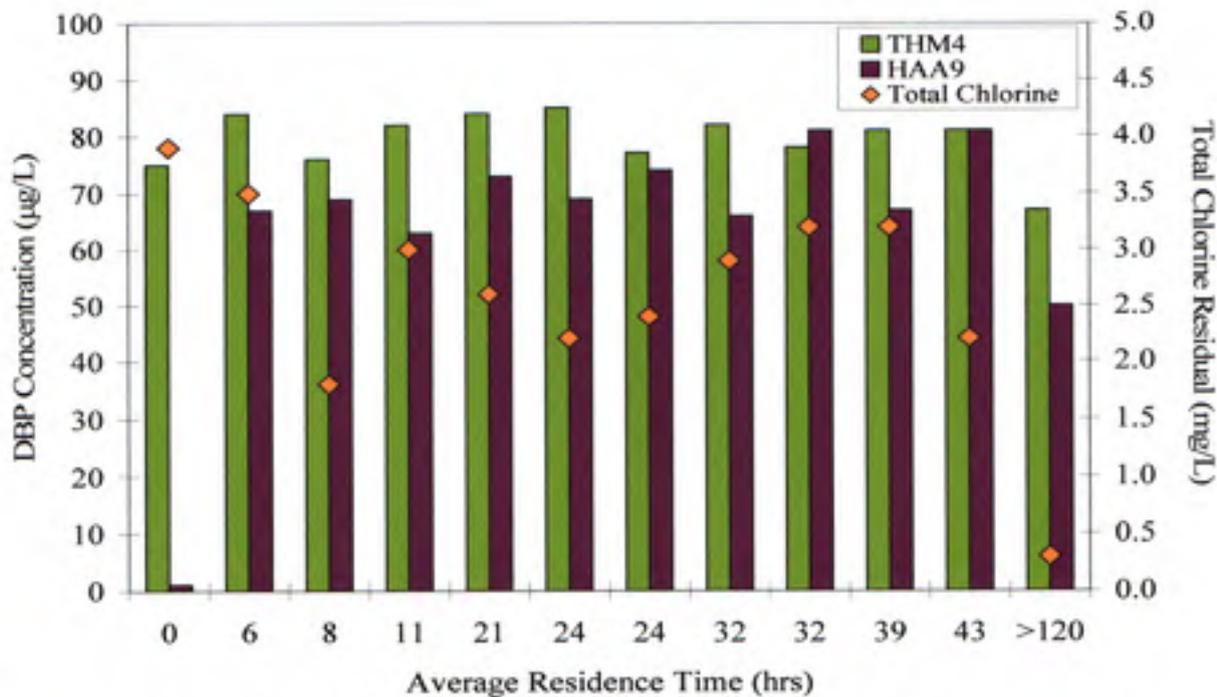


Figure A.28 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 6/11/03

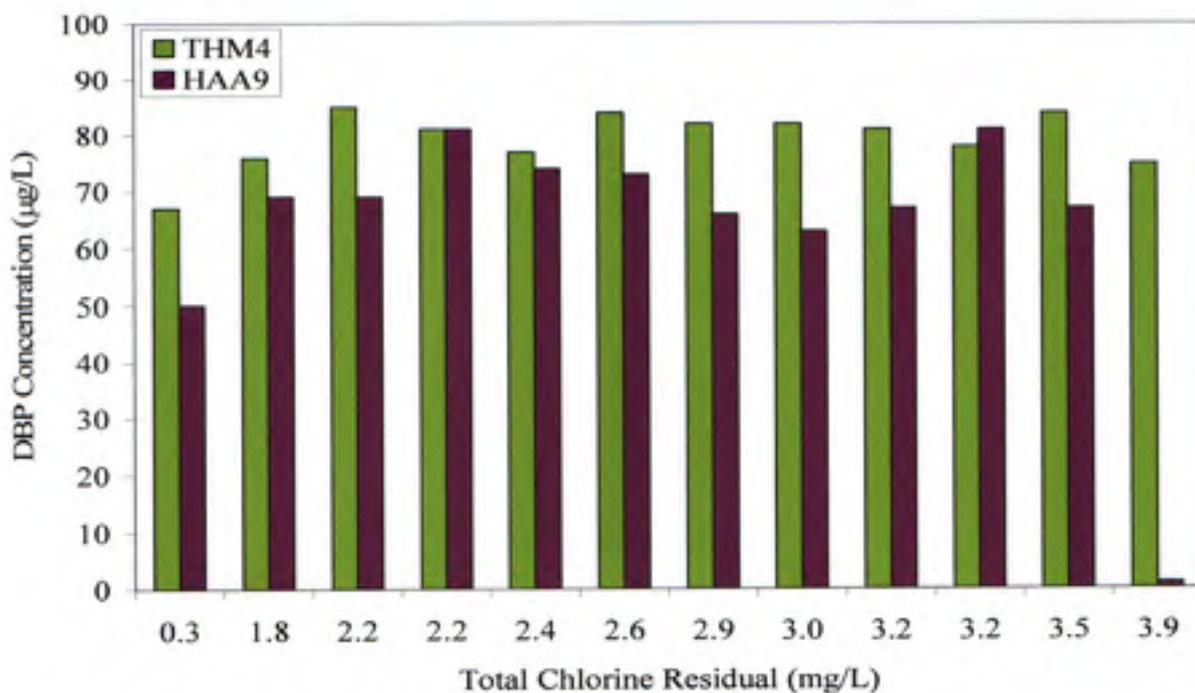


Figure A.29 THM4 and HAA9 versus total chlorine residual for Utility C for 6/11/03

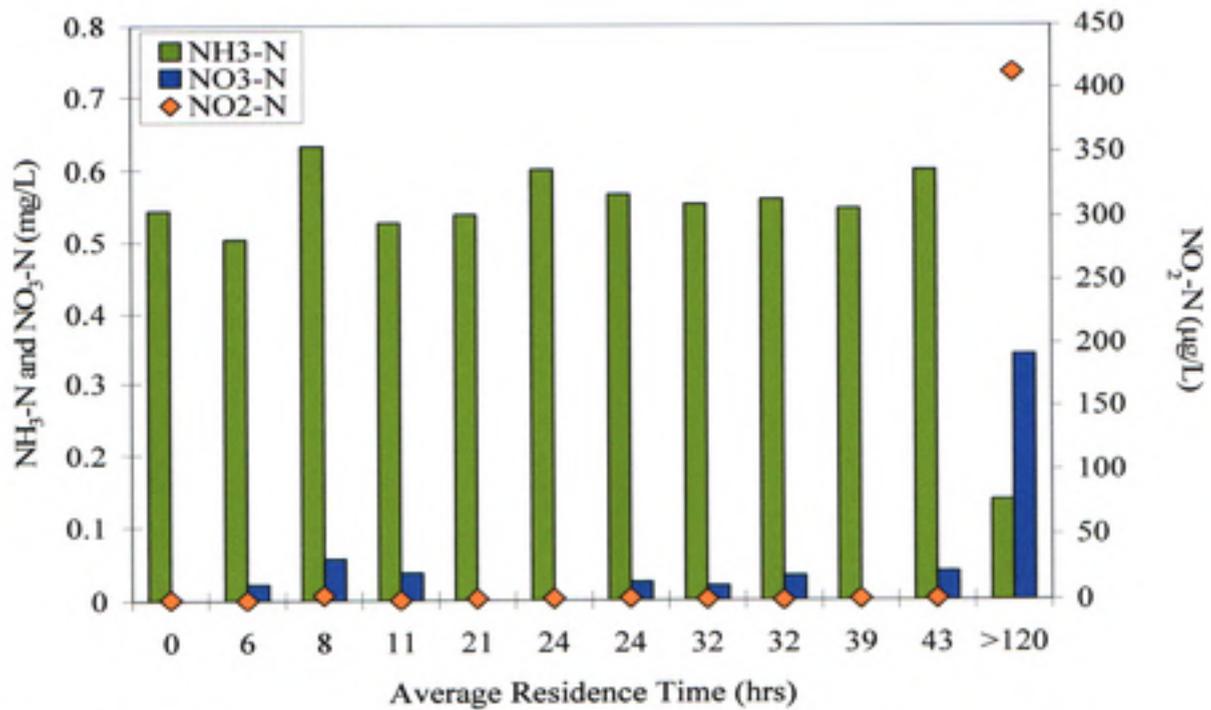


Figure A.30 Nitrogen species versus average residence time for Utility C for 6/11/03

Table A.25

pH, temperature and chlorine data for Utility C for 8/12/03

Sample ID	Temperature (°C)	pH	Total Cl <sub>2</sub> (mg/L)
POE	27	7.0	3.30
1	26	6.9	3.60
2	27	7.2	2.90
3	27	7.2	2.20
4	27	7.2	2.90
8	27	7.2	3.40
9	27	7.2	3.00
10	27	7.4	3.80
13	27	7.4	3.50
20	26	7.5	0.38
15	28	7.7	1.30
1721	28	7.6	2.30

Table A.26

Organic carbon, microbiological and nitrogen data for Utility C for 8/12/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)
POE	211	3.31	0.064	7.0E+00	0.637	0.450	0.040
1		3.2	0.062	1.2E+01	0.717	2.24	0.057
2		3.18	0.062	1.0E+01	0.716	2.05	0.056
3		3.160	0.060	5.0E+00	0.719	2.37	0.061
4		3.2	0.061	2.4E+01	0.698	0.45	0.056
8		3.18	0.062	6.0E+00	0.680	0.63	0.049
9		3.2	0.060	1.3E+01	0.686	0.42	0.057
10		3.19	0.063	8.0E+00	0.693	0.18	0.040
13		3.18	0.064	1.0E+00	0.655	0.54	0.039
20		3.15	0.056	1.9E+02	0.714	19.6	0.188
15		3.11	0.053	1.8E+03	0.356	338	0.470
1721		3.17	0.060	3.8E+01	0.700	7.20	0.090

Table A.27

Trihalomethane (THM) data (in µg/L) for Utility C for 8/12/03

Sample ID	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	THM4
POE	80	7	1	<1	88
1	65	7	1	<1	73
2	79	8	1	<1	88
3	82	9	<1	<1	91
4	70	8	1	<1	79
8	74	8	<1	<1	82
9	79	8	1	<1	88
10	76	8	1	<1	85
13	72	7	1	<1	80
20	76	9	1	<1	86
15	62	9	1	<1	72
1721	73	8	1	<1	82

Table A.28

Haloacetic acid (HAA) data (in µg/L) for Utility C for 8/12/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
POE	7	3	37	4	2	31	4	<1	<1	88
1	1	3	38	5	<1	32	3	<1	<1	82
2	<2	3	36	4	2	31	4	<1	<1	80
3	<2	3	39	4	1	29	4	<1	<1	80
4	3	3	37	4	<1	31	3	1	<1	82
8	<2	3	37	4	2	32	5	<1	<1	83
9	<2	3	37	4	2	30	4	<1	<1	80
10	12	3	38	5	<1	32	3	<1	<1	93
13	5	3	40	5	2	33	5	<1	<1	93
20	<2	4	38	5	2	34	2	<1	<1	85
15	<2	3	30	4	1	30	4	<1	<1	72
1721	10	3	36	4	1	31	4	<1	<1	89

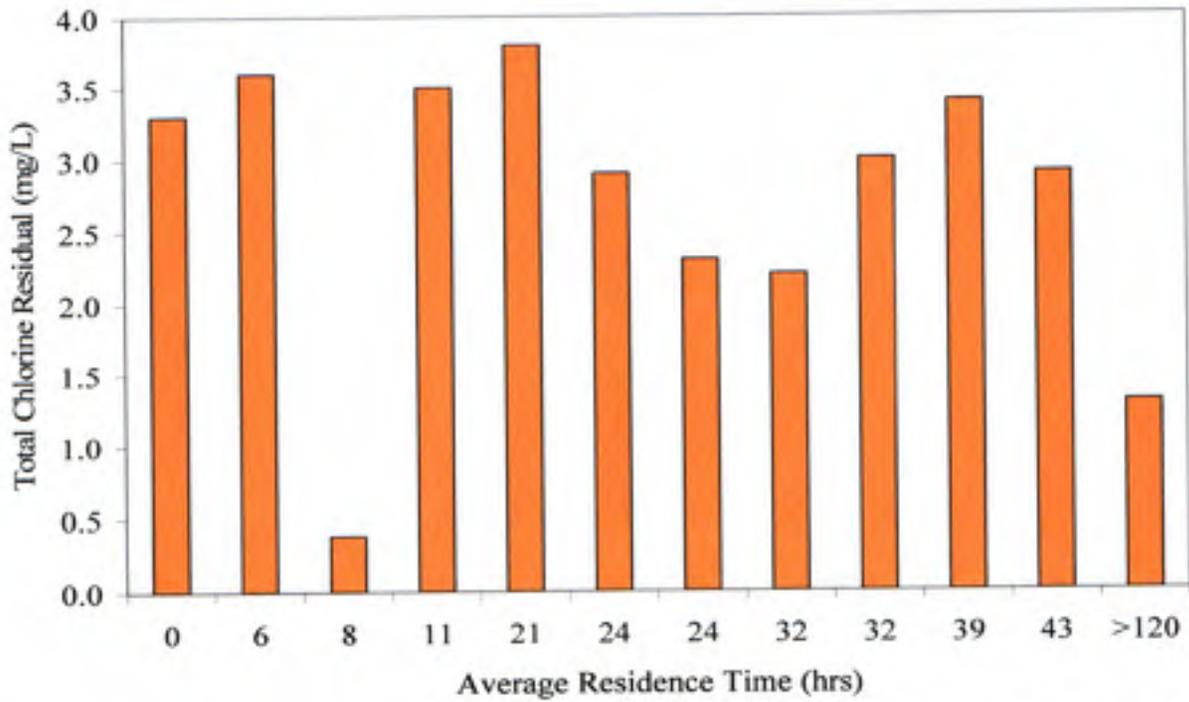


Figure A.31 Total chlorine residual versus average residence time for Utility C for 8/12/03

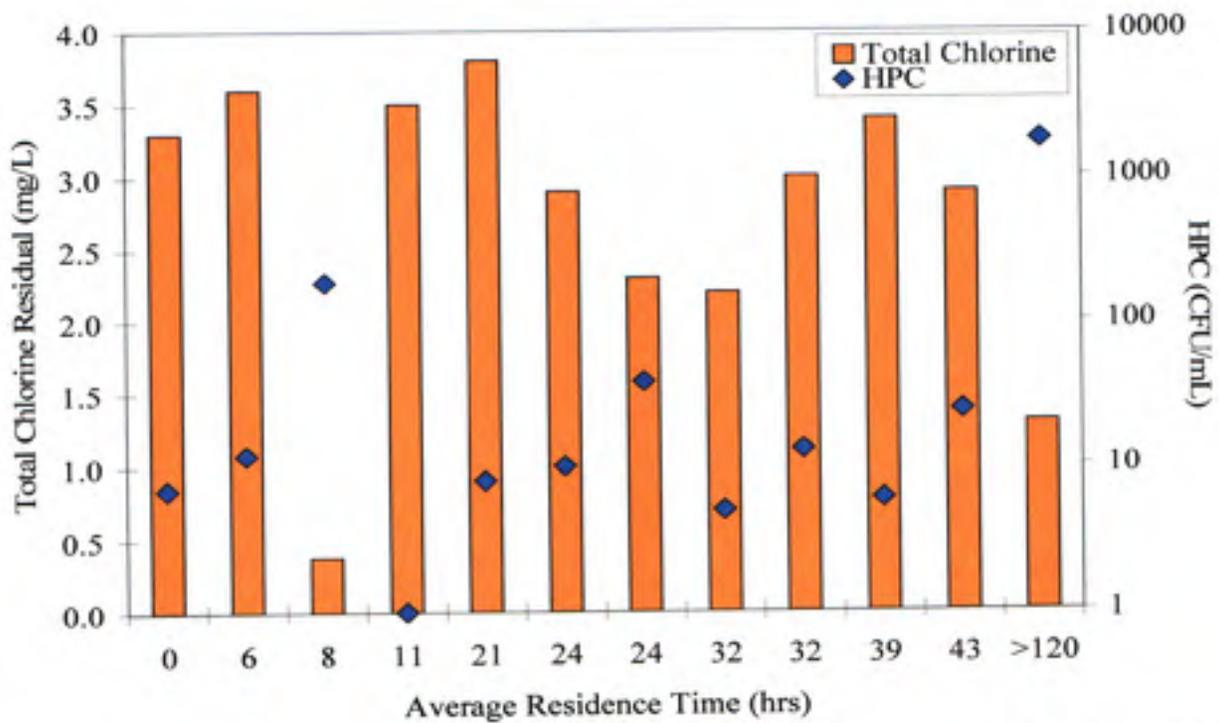


Figure A.32 Total chlorine residual and HPC versus average residence time for Utility C for 8/12/03

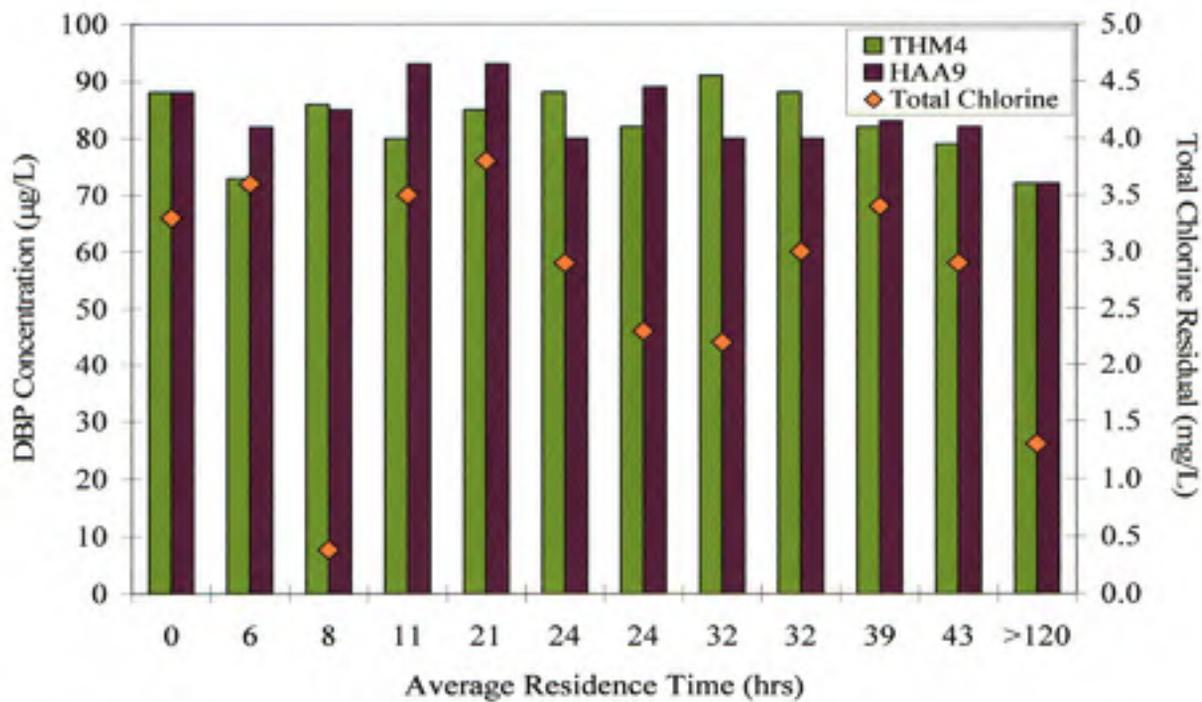


Figure A.33 THM4, HAA9 and total chlorine residual versus average residence time for Utility C for 8/12/03

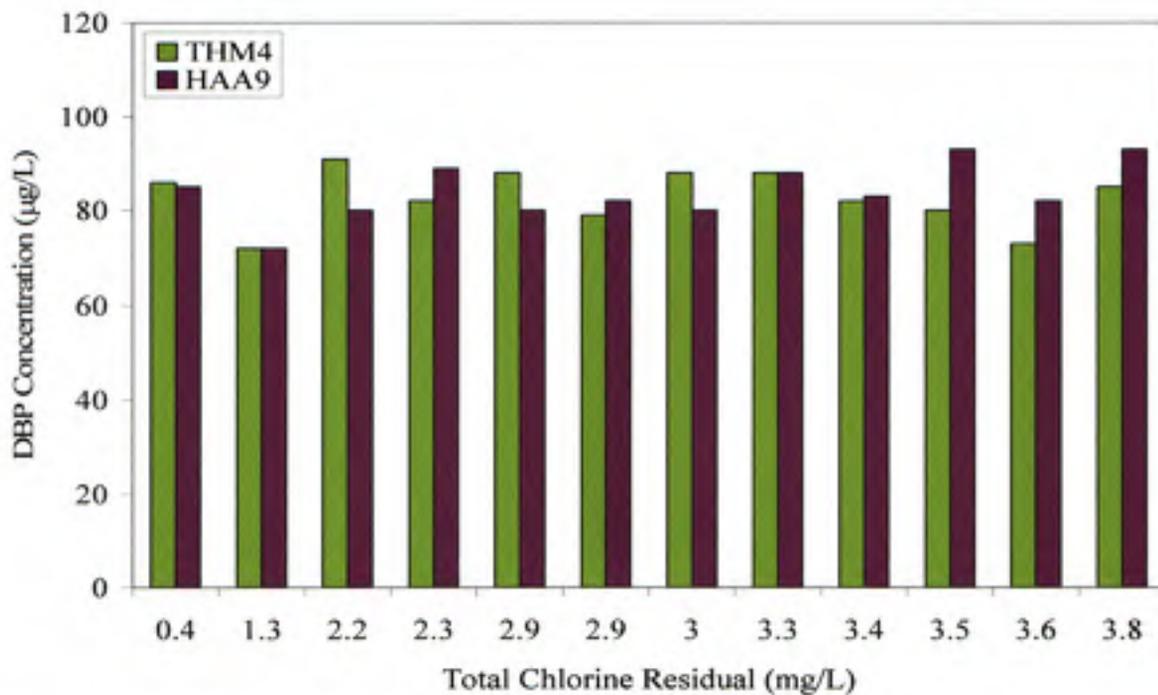


Figure A.34 THM4 and HAA9 versus total chlorine residual for Utility C for 8/12/03

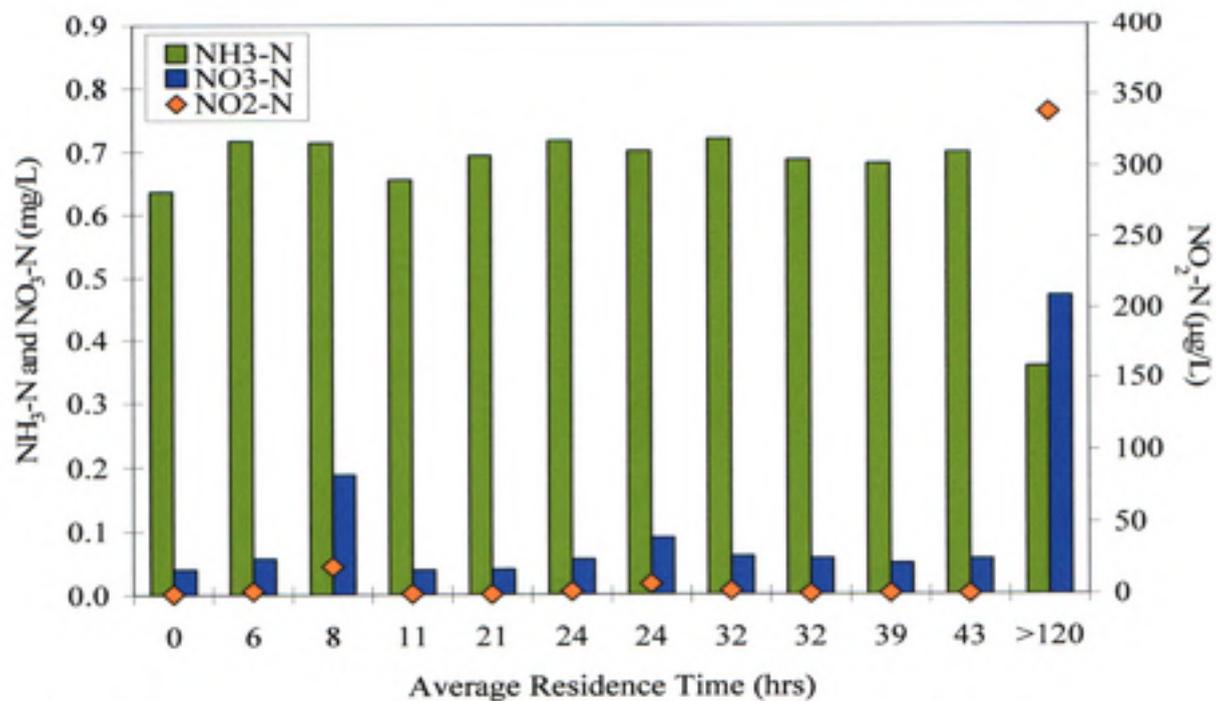


Figure A.35 Nitrogen species versus average residence time for Utility C for 8/12/03

**APPENDIX B**

**Utility A**

Table B.1

pH, temperature and chlorine data for Utility A for 10/16/02

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
EP001	13	9.1	2.5	3.1
MR001	13	9.1	0.9	1.1
RD002	18	9.3	1.5	1.7
RD004	18	9.1	0.6	0.9
RD005	16	9.6	1.4	1.6
RD007	19	9.1	1.6	1.8
RD013	18	9.2	1.6	1.8
RD018	16	9.4	1.3	1.6
RD020	16	9.1	1.2	1.4
RD025	17	9.1	0.1	0.1
RD027	17	9.0	0.3	0.5
RD028	17	9.1	0.8	0.8
RD029	17	8.0	0.7	0.9

Table B.2

Organic carbon and microbiological data for Utility A for 10/16/02

Sample ID	AOC (mg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
EP001	740	2.40	0.026	4.0E+01
MR001		*	0.021	
RD002		2.23	0.019	<10
RD004		2.05	0.023	3.6E+02
RD005		2.26	0.024	1.3E+02
RD007		2.27	0.018	1.0E+01
RD013		2.26	0.029	<10
RD018		2.30	0.029	<10
RD020		1.90	0.027	2.4E+03
RD025		1.58	0.028	1.6E+04
RD027		1.89	0.026	5.8E+03
RD028		1.95	0.023	2.0E+02
RD029		2.15	0.023	2.0E+01

\* Sample and duplicate broke during shipping

Table B.3

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility A for 10/16/02

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2^*$	$\text{CHBr}_2\text{Cl}^*$	$\text{CHBr}_3$	THM4
EP001	38	10	3	<.1	51
MR001	88	26	11	2	127
RD002	72**	23	10	2	107
RD004	81	26	11	3	120
RD005	58	20	8	2	88
RD007	56	19	8	2	85
RD013	53	18	8	1	81
RD018	58	20	8	2	88
RD020	118	30	13	3	164
RD025	116	43	24	10	194
RD027	103	28	12	3	146
RD028	114	29	13	3	159
RD029	87	26	11	2	126

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

\*\* Duplicate broke during shipping

Table B.4

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility A for 10/16/02

Sample ID	ClAA*	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
EP001	16	<2	15	3	<2	2	3	<2	**	39
MR001	5	<2	21	6	2	4	4	<2	**	42
RD002	6	<2	18	5	<2	3	4	2	**	35
RD004	4	<2	18	5	<2	3	4	<2	**	34
RD005	10	<2	17	5	<2	3	3	<2	**	38
RD007	6	<2	17	5	<2	3	3	<2	**	34
RD013	9	<2	16	5	<2	3	3	<2	**	36
RD018	9	<2	19	5	<2	3	4	<2	**	40
RD020	2	<2	5	<2	<2	6	4	<2	**	18
RD025	<2	<2	<2	<2	<2	<2	3	<2	**	3
RD027	<2	<2	3	<2	<2	6	4	<2	**	13
RD028	4	<2	5	<2	<2	6	4	<2	**	20
RD029	4	<2	21	7	2	4	4	2	**	42

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

\*\* Br<sub>3</sub>AA was not quantifiable; but levels are expected to be below detection limit

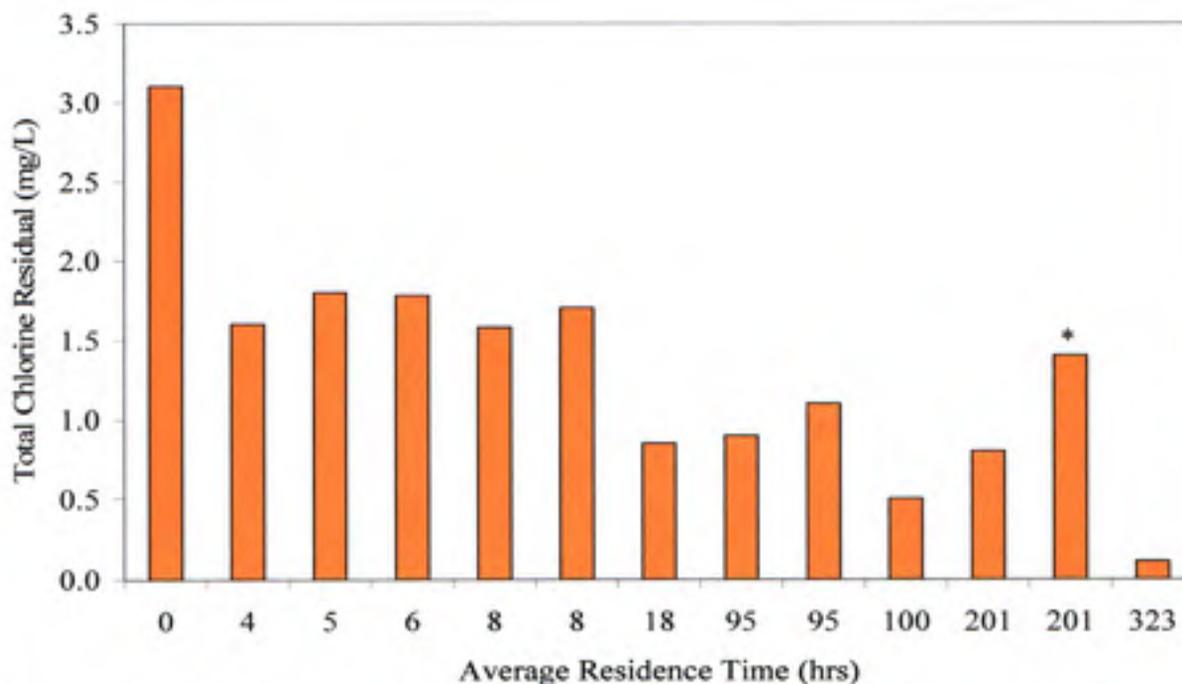


Figure B.1 Total chlorine residual versus average residence time for Utility A for 10/16/02. (\* indicates a location after rechlorination)

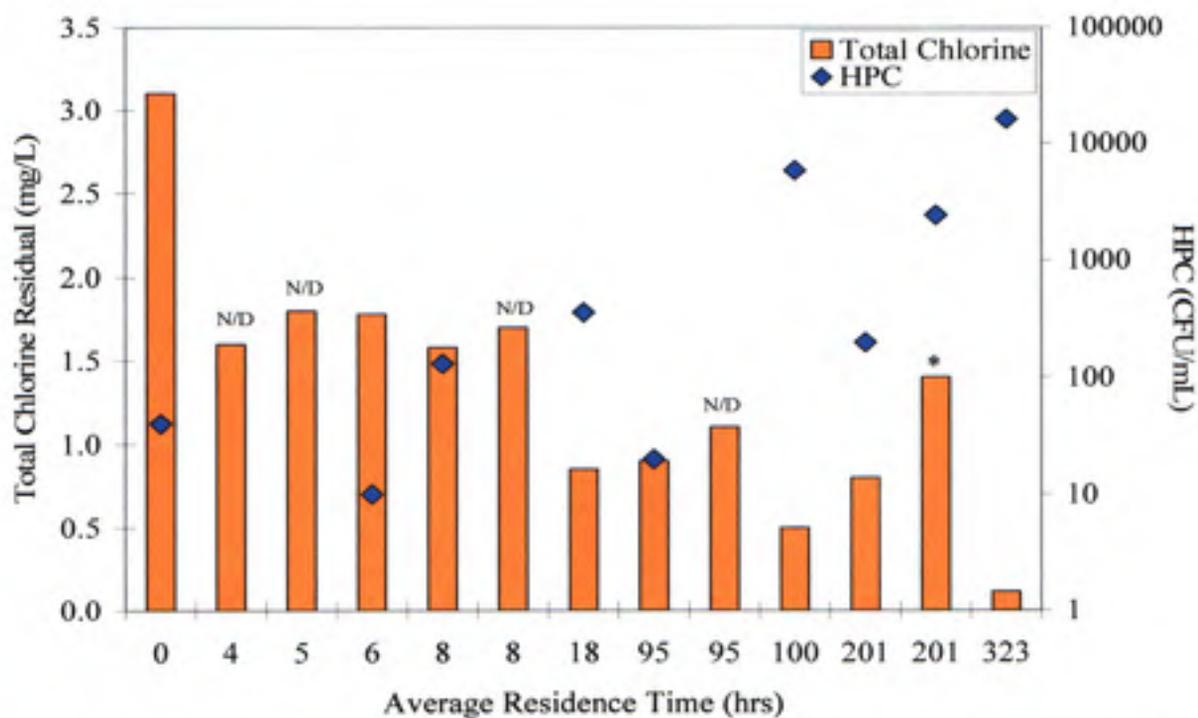


Figure B.2 Total chlorine residual and HPC versus average residence time for Utility A for 10/16/02. (\* indicates a location after rechlorination)

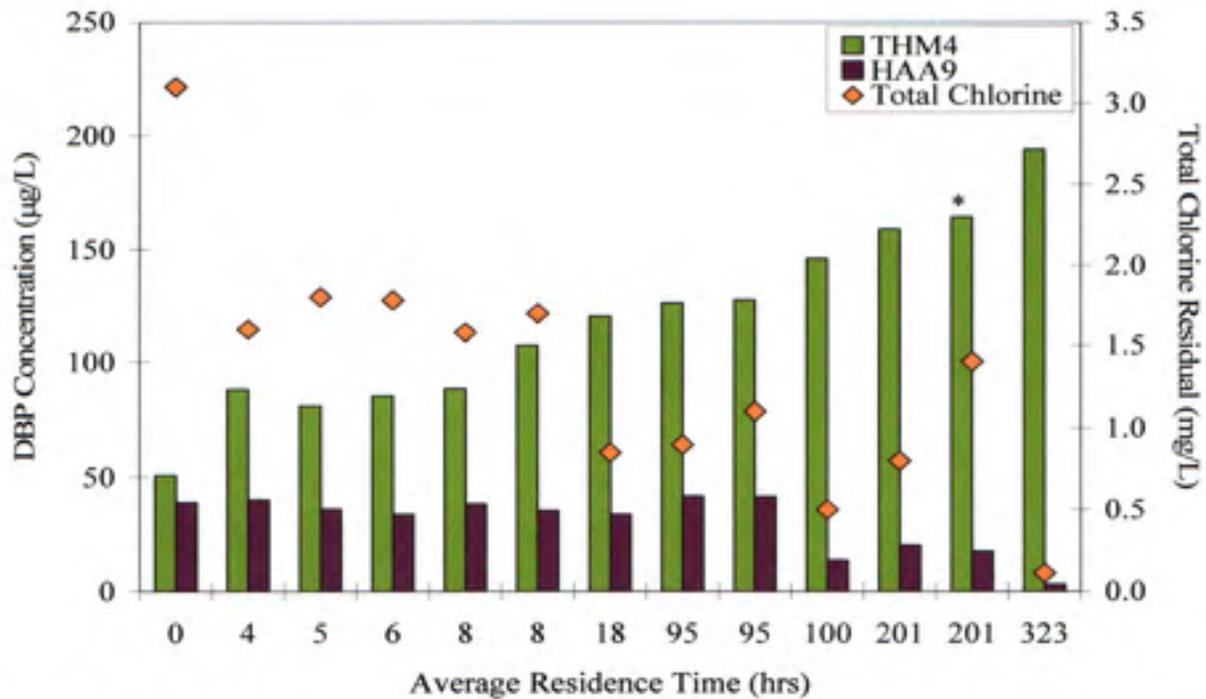


Figure B.3 THM4, HAA9 and total chlorine residual versus average residence time for Utility A for 10/16/02. (\* indicates a location after rechlorination)

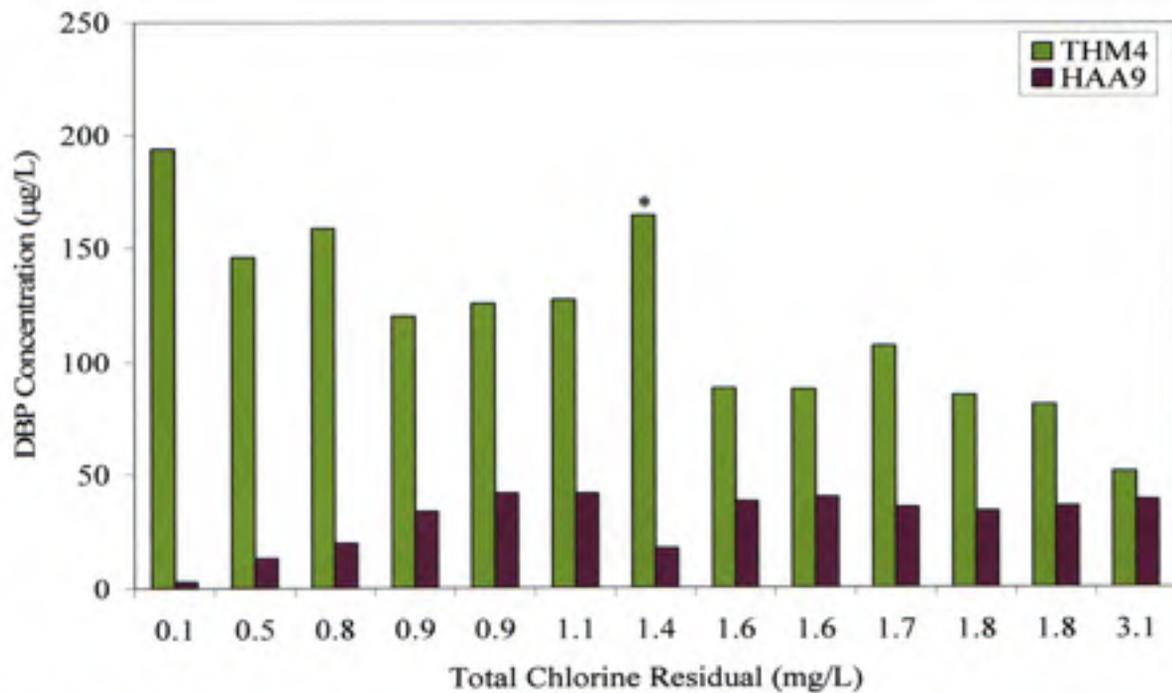


Figure B.4 THM4 and HAA9 versus total chlorine residual for Utility A for 10/16/02. (\* indicates a location after rechlorination)

Table B.5

pH, temperature and chlorine data for Utility A for 12/03/02

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
EP001	5.6	9.5	2.4	2.6
MR001	7.7	9.1	1.1	1.1
RD002	10.0	9.2	1.6	1.7
RD004	16.6	9.2	1.2	1.2
RD005	11.1	9.3	1.1	1.3
RD007	20.0	9.3	2.0	2.3
RD013	11.1	9.2	1.3	1.5
RD018	11.1	9.2	1.9	2.2
RD020	11.6	9.2	0.5	0.6
RD025	12.2	9.2	0.0	0.0
RD027	11.6	9.1	0.4	0.5
RD028	11.6	9.0	1.1	1.2
RD029	10.0	9.1	1.2	1.4

Table B.6

Organic carbon and microbiological data for Utility A for 12/03/02

Sample ID	AOC (mg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
EP001	453	1.24	0.029	4.5E+02
MR001		1.21	0.031	3.4E+03
RD002		1.15	0.0304	1.7E+02
RD004		1.17	0.0296	6.8E+02
RD005		1.23	0.0301	5.5E+02
RD007		1.12	0.0301	8.0E+01
RD013		1.19	0.0305	8.0E+02
RD018		1.26	0.0299	9.0E+01
RD020		1.44 *	0.0347	3.0E+03
RD025		1.42	0.0356	1.9E+04
RD027		1.23	0.0306	3.0E+03
RD028		1.48	0.0354	7.1E+03
RD029		1.41	0.0296	1.7E+03

\* Duplicate broke during shipping

Table B.7

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility A for 12/03/02

Sample ID	$\text{CHCl}_3^*$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
EP001	10	3	1	<1	13
MR001	40	12	4	<1	57
RD002	14	6	2	<1	22
RD004	29	11	4	<1	44
RD005	35	9	3	<1	47
RD007	14	5	2	<1	21
RD013	17	6	2	<1	25
RD018	16	6	2	<1	23
RD020	70	16	5	<1	91
RD025	110	35	16	2	163
RD027	61	15	5	<1	81
RD028	62	15	4	<1	81
RD029	29	9	3	<1	41

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

Table B.8

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility A for 12/03/02

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
EP001	<2	<2	5	<2	<2	<2	<2	<2	<2	5
MR001	3	<2	11	3	<2	2	3	<2	<2	22
RD002	4	<2	5	<2	<2	<2	<2	<2	<2	9
RD004	2	<2	7	2	<2	<2	2	<2	<2	14
RD005	3	<2	9	2	<2	<2	2	<2	<2	16
RD007	5	<2	5	<2	<2	<2	2	<2	<2	12
RD013	5	<2	5	<2	<2	<2	2	3	<2	15
RD018	3	<2	6	<2	<2	<2	<2	<2	<2	9
RD020	4	<2	12	3	<2	5	3	<2	<2	27
RD025	<2	<2	<2	<2	<2	3	3	<2	<2	6
RD027	<2	<2	6	<2	<2	4	3	<2	<2	13
RD028	<2	<2	11	2	<2	5	3	<2	<2	21
RD029	2	<2	11	3	<2	<2	<2	<2	2	18

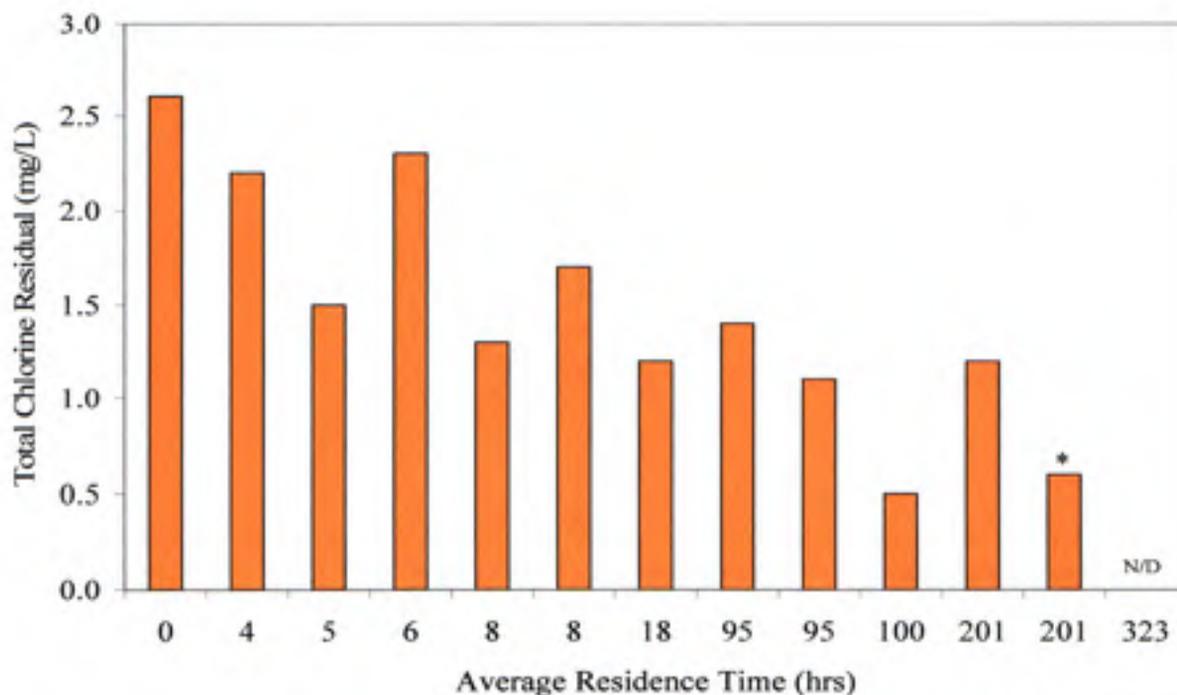


Figure B.5 Total chlorine residual versus average residence time for Utility A for 12/03/02. (\* indicates a location after rechlorination)

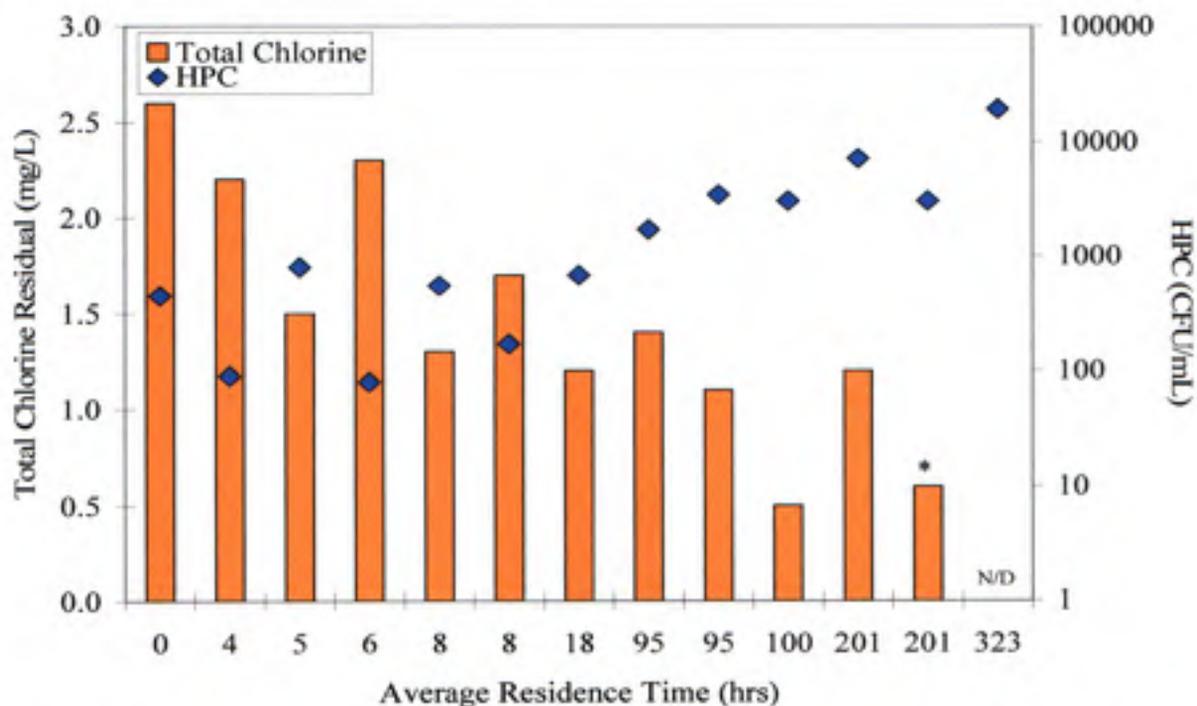


Figure B.6 Total chlorine residual and HPC versus average residence time for Utility A for 12/03/02. (\* indicates a location after rechlorination)

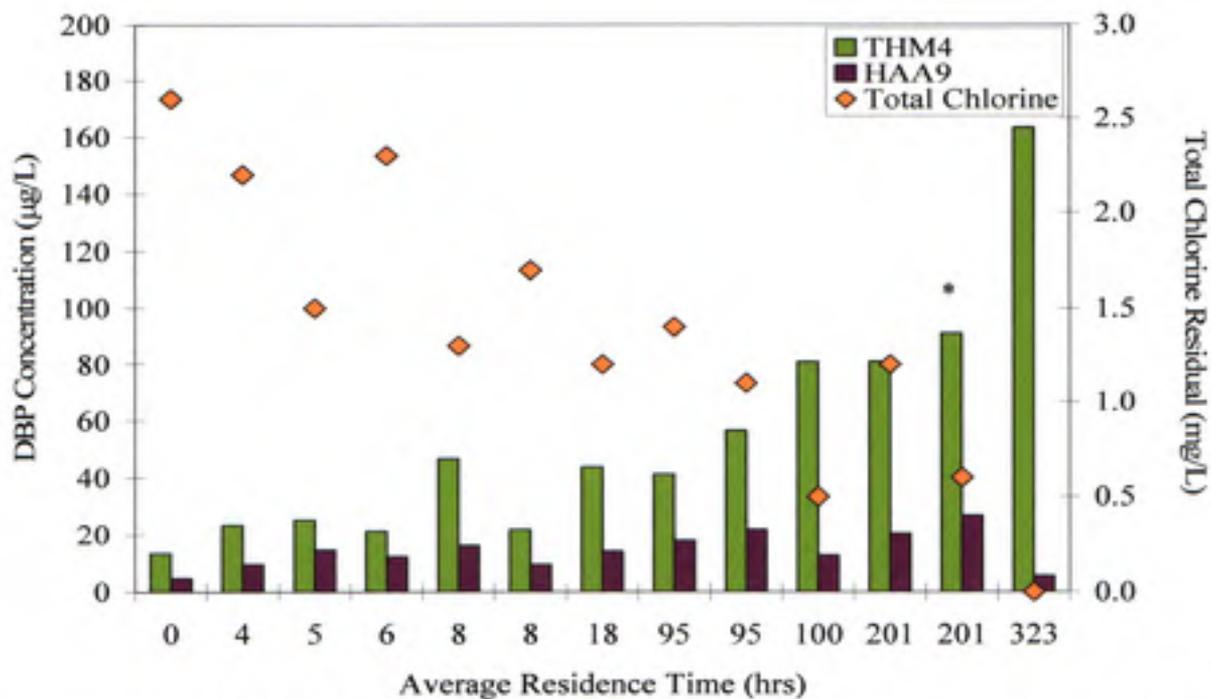


Figure B.7 THM4, HAA9 and total chlorine residual versus average residence time for Utility A for 12/03/02. (\* indicates a location after rechlorination)

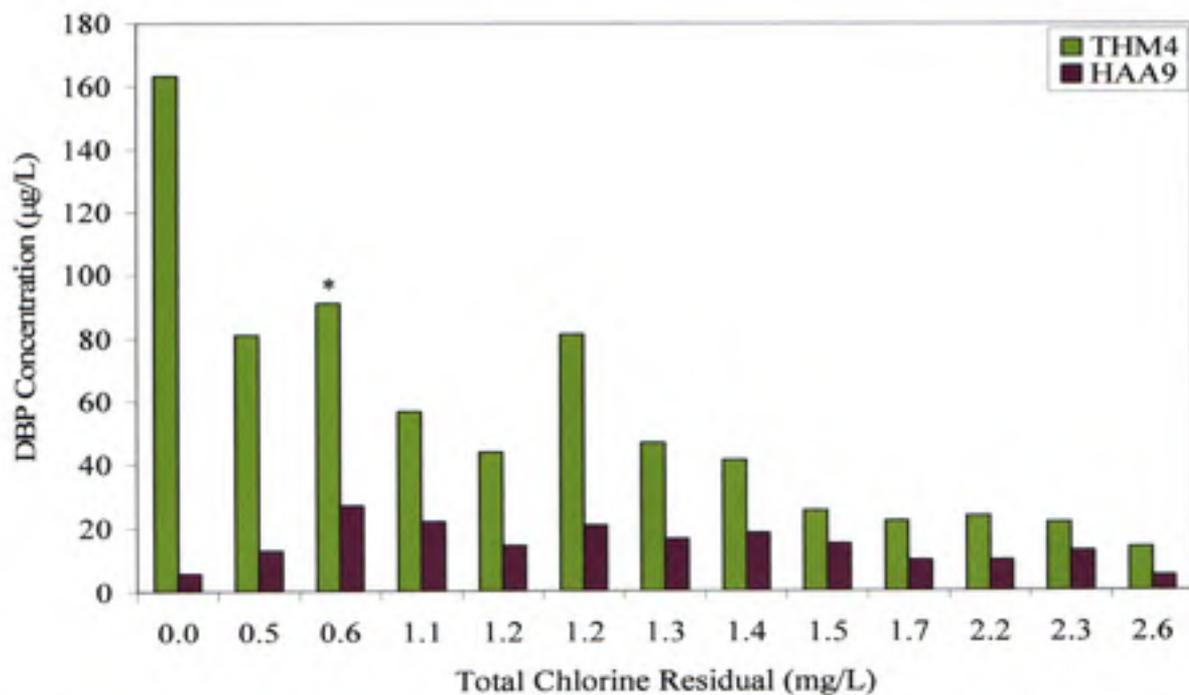


Figure B.8 THM4 and HAA9 versus total chlorine residual for Utility A for 12/03/02. (\* indicates a location after rechlorination)

Table B.9

pH, temperature and chlorine data for Utility A for 1/07/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
EP001	6.1	8.7	2.5	3.1
MR001	8.8	8.7	1.7	1.8
RD002	11.1	8.7	2.3	2.5
RD004	12.2	8.9	1.8	1.9
RD005	13.8	8.7	2.2	2.2
RD007	17.7	8.9	2.2	2.5
RD013	12.7	8.7	2.0	2.3
RD018	8.8	8.6	3.3	3.4
RD020	8.3	8.8	2.0	2.0
RD025	10.0	8.8	1.3	1.4
RD027	8.8	8.9	1.3	1.5
RD028	10.0	8.9	1.5	1.9
RD029	13.8	8.8	1.5	1.9

Table B.10

Organic carbon and microbiological data for Utility A for 1/07/03

Sample ID	AOC (mg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
EP001	270	1.19	0.029	NA
MR001				1.9E+02
RD002				4.0E+01
RD004				1.0E+01
RD005				5.0E+00
RD007				<10
RD013				<10
RD018				5.0E+00
RD020				<10
RD025				5.0E+00
RD027				1.0E+01
RD028				2.9E+02
RD029				2.0E+01

Table B.11

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility A for 1/07/03

Sample ID	$\text{CHCl}_3^*$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
EP001	7	4	2	<1	13
MR001	32	16	8	1	58
RD002	16	10	5	<1	31
RD004	30	16	8	1	54
RD005	16	10	5	1	32
RD007	13	9	5	<1	26
RD013	13	9	5	<1	27
RD018	11	8	4	<1	23
RD020	40	19	10	2	71
RD025	73	23	11	2	108
RD027	46	19	9	1	76
RD028	39	19	10	2	69
RD029	31	16	8	1	56

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

Table B.12

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility A for 1/07/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA*	BrClAA*	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
EP001	3	<2	4	<2	<2	<2	3	2	<2	13
MR001	3	2	8	3	<2	2	4	2	<2	24
RD002	6	<2	5	2	<2	<2	3	2	<2	18
RD004	3	<2	7	3	<2	<2	3	2	<2	18
RD005	5	<2	5	2	<2	<2	3	2	<2	17
RD007	3	<2	5	<2	<2	<2	3	2	<2	13
RD013	3	<2	5	<2	<2	<2	3	2	<2	13
RD018	3	<2	5	<2	<2	<2	3	2	<2	13
RD020	4	<2	8	3	<2	3	4	3	<2	24
RD025	4	<2	11	4	2	4	5	3	<2	32
RD027	<2	<2	8	3	<2	3	4	2	<2	21
RD028	4	<2	8	3	<2	3	4	3	<2	25
RD029	4	<2	7	3	<2	<2	3	2	<2	19

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

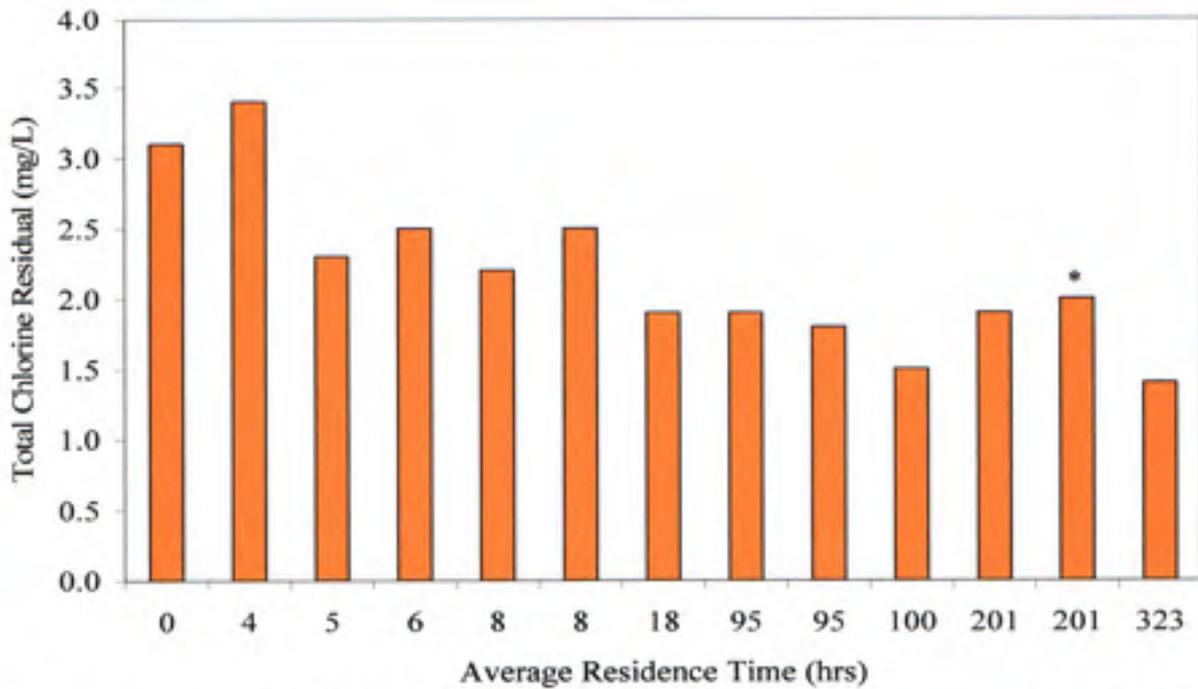


Figure B.9 Total chlorine residual versus average residence time for Utility A for 1/07/03. (\* indicates a location after rechlorination)

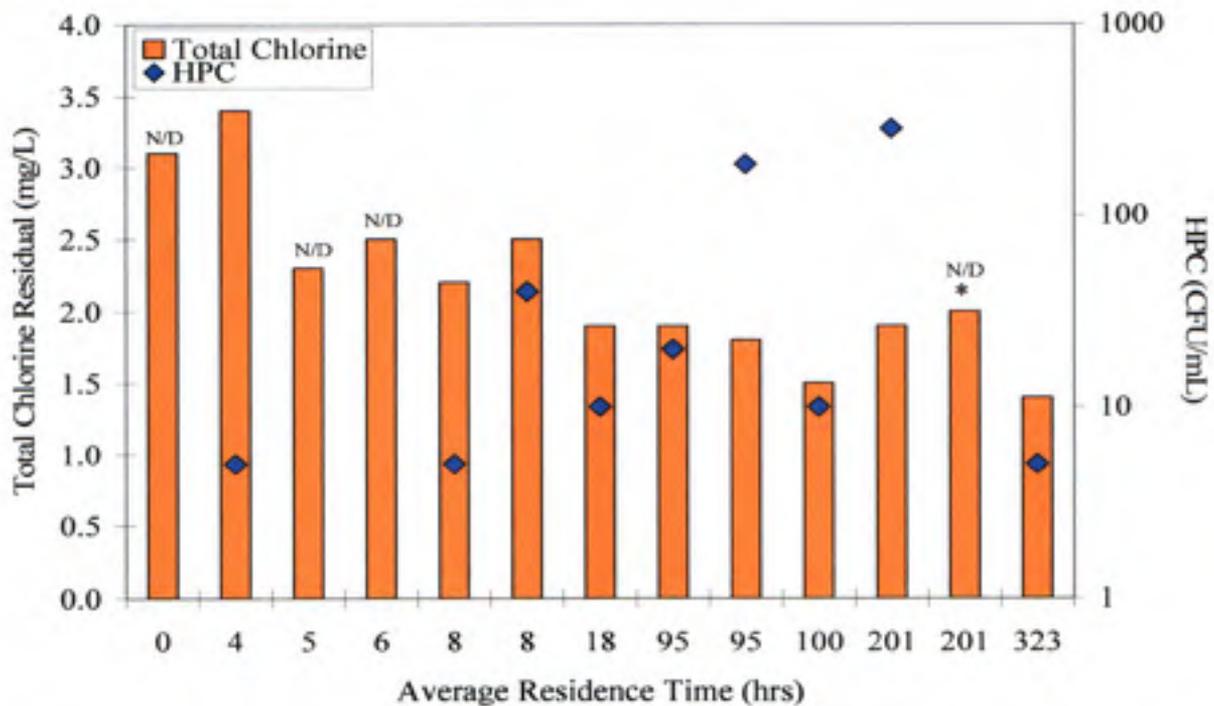


Figure B.10 Total chlorine residual and HPC versus average residence time for Utility A for 1/07/03. (\* indicates a location after rechlorination)

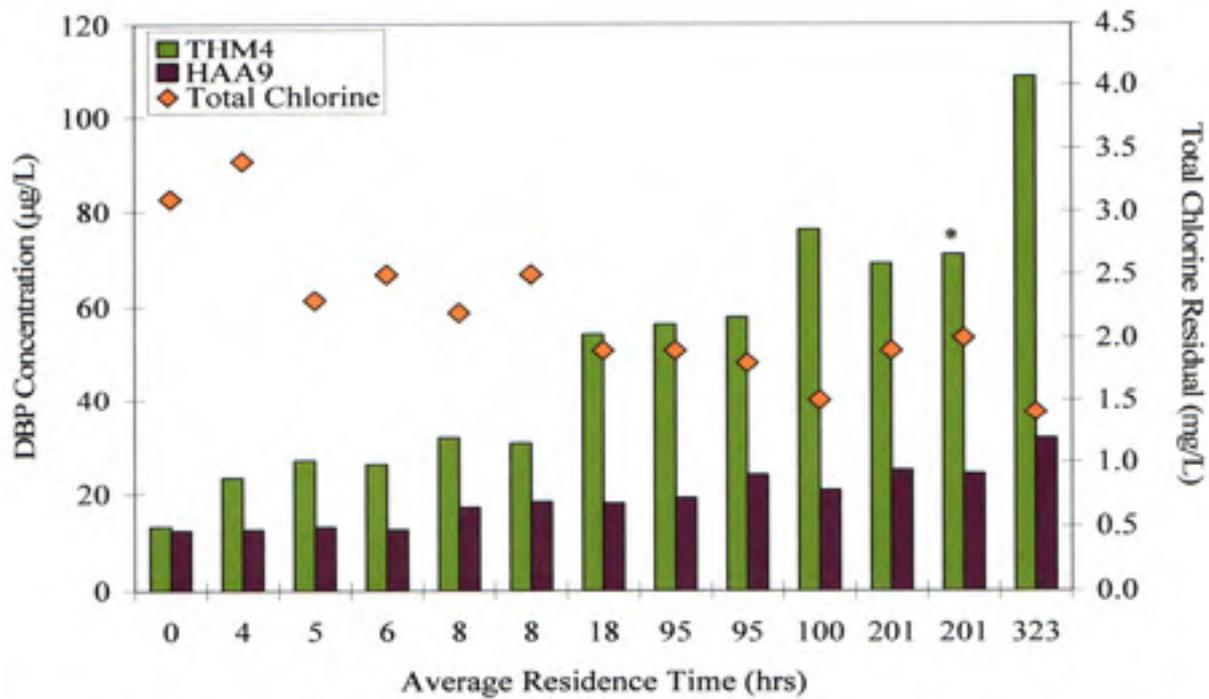


Figure B.11 THM4, HAA9 and total chlorine residual versus average residence time for Utility A for 1/07/03. (\* indicates a location after rechlorination)

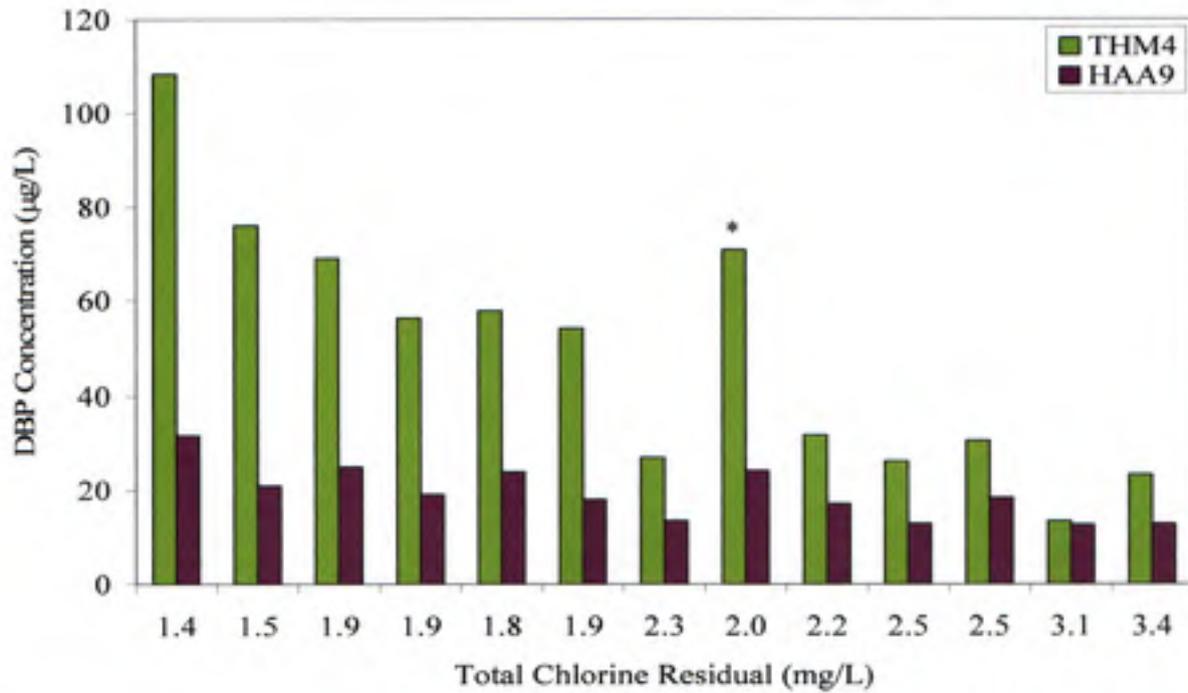


Figure B.12 THM4 and HAA9 versus total chlorine residual for Utility A for 1/07/03. (\* indicates a location after rechlorination)

Table B.13  
pH, temperature and chlorine data for Utility A for 2/25/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
EP001	4.0	9.1	2.7	3.6
MR001	2.5	9.0	1.4	1.4
RD002	4.5	8.9	1.8	1.9
RD004	10	9.0	1.0	1.2
RD005	6.5	8.9	1.5	2.1
RD007	19	8.9	1.9	2.1
RD013	6.5	9.0	1.8	2.0
RD018	7.0	8.9	1.9	2.1
RD020	3.5	9.1	1.3	1.4
RD025	6.0	9.0	1.4	1.5
RD027	7.0	8.9	1.3	1.4
RD028	4.0	9.0	1.3	1.3
RD029	9.5	8.9	1.9	2.1

Table B.14  
Organic carbon and microbiological data for Utility A for 2/25/03

Sample ID	AOC (mg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
EP001	711	2.80	0.04	< 10
MR001				5.0E+01
RD002				2.3E+02
RD004				< 10
RD005				< 10
RD007				7.0E+01
RD013				5.0E+00
RD018				5.0E+00
RD020				4.5E+01
RD025				1.1E+02
RD027				2.0E+01
RD028				3.6E+02
RD029				NA

Table B.15

Trihalomethane (THM) data (in µg/L) for Utility A for 2/25/03

Sample ID	CHCl <sub>3</sub> *	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	THM4
EP001	31	6	1	<1	38
MR001	40	17	7	<1	64
RD002	50	14	3	<1	67
RD004	40	15	6	1	62
RD005	49	14	3	<1	66
RD007	47	14	2	<1	63
RD013	48	13	2	<1	63
RD018	26	8	2	<1	35
RD020	26	15	9	2	52
RD025	65	21	9	1	97
RD027	30	16	9	2	57
RD028	26	15	9	2	51
RD029	50	15	3	<1	69

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

Table B.16

Haloacetic acid (HAA) data (in µg/L) for Utility A for 2/25/03

Sample ID	ClAA*	BrAA	Cl <sub>2</sub> AA	BrClAA*	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA*	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
EP001	8	<2	19	<2	<2	4	2	<2	<2	33
MR001	3	<2	13	3	<2	3	4	2	<2	28
RD002	7	<2	21	3	<2	6	4	<2	<2	41
RD004	6	<2	14	3	<2	3	4	2	<2	32
RD005	6	<2	22	3	<2	6	4	<2	<2	41
RD007	8	<2	22	3	<2	6	4	<2	<2	42
RD013	10	<2	21	3	<2	6	4	<2	<2	44
RD018	10	<2	22	3	<2	6	4	<2	<2	46
RD020	6	<2	7	3	<2	<2	4	3	<2	21
RD025	6	<2	13	4	<2	4	4	2	<2	33
RD027	7	<2	8	3	2	2	4	3	<2	28
RD028	7	<2	7	3	2	<2	4	3	<2	25
RD029	10	<2	21	3	<2	6	4	<2	<2	44

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

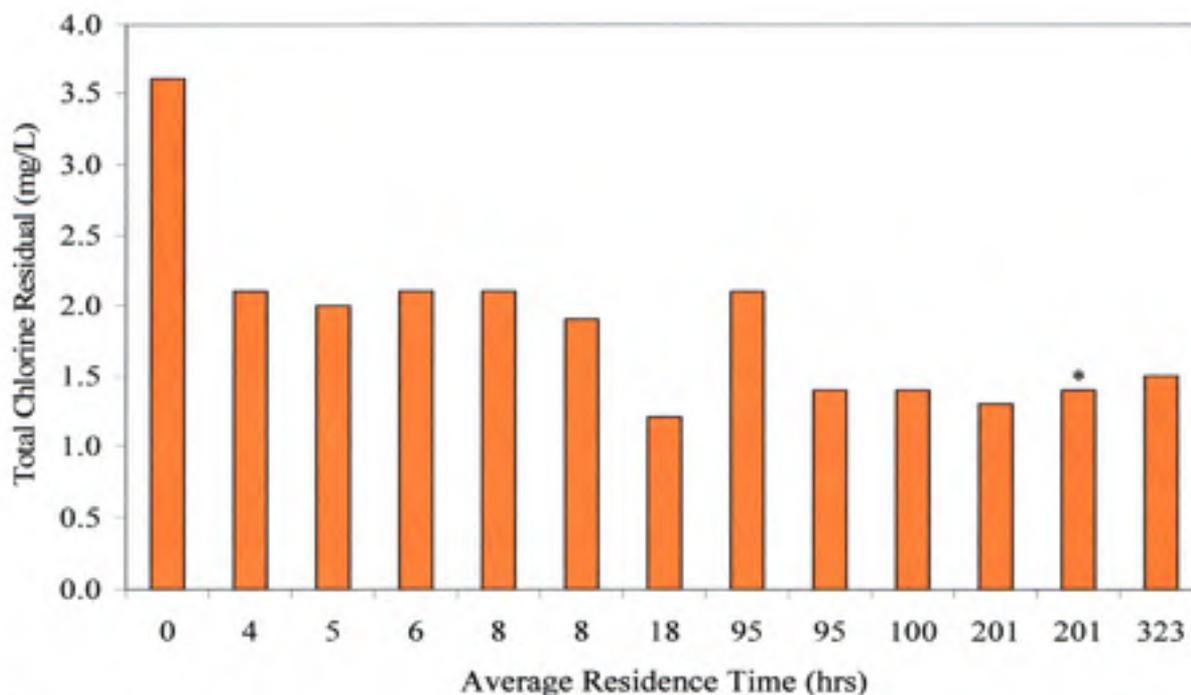


Figure B.13 Total chlorine residual versus average residence time for Utility A for 2/25/03. (\* indicates a location after rechlorination)

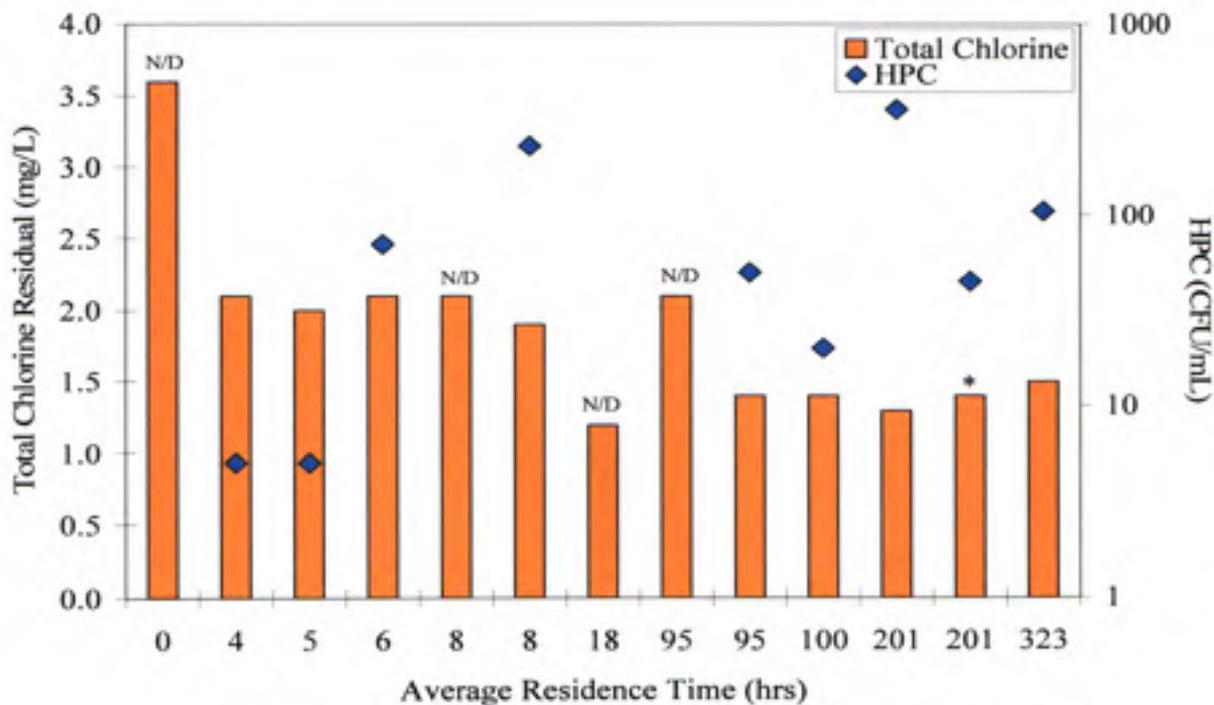


Figure B.14 Total chlorine residual and HPC versus average residence time for Utility A for 2/25/03. (\* indicates a location after rechlorination)

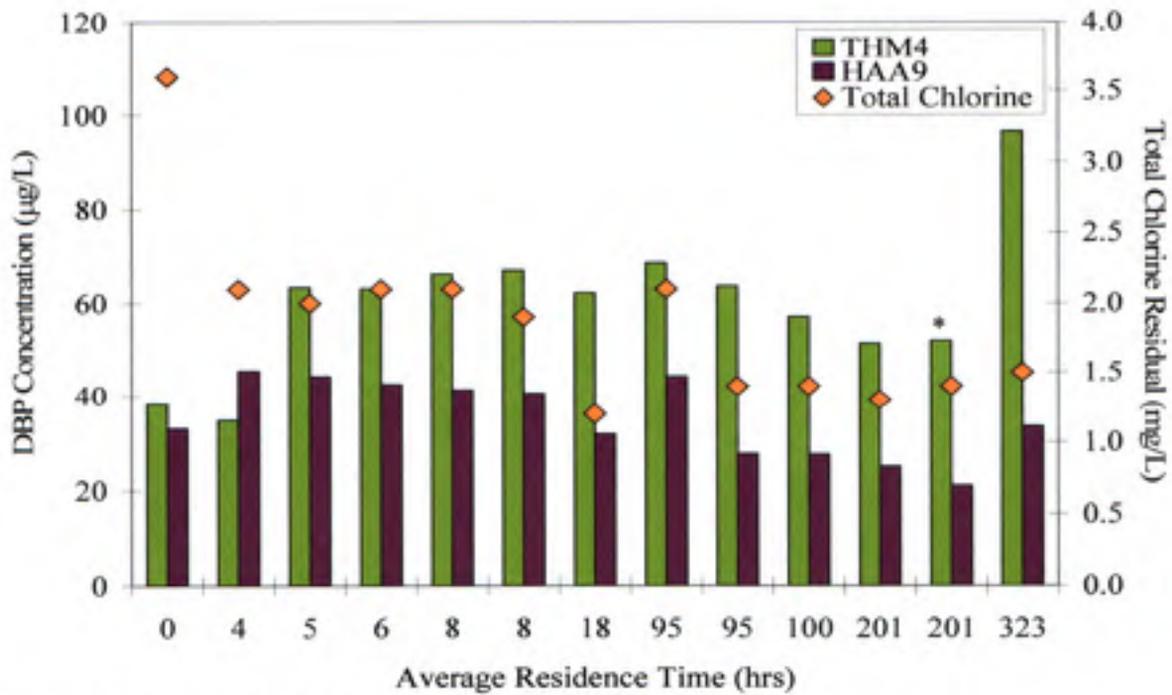


Figure B.15 THM4, HAA9 and total chlorine residual versus average residence time for Utility A for 2/25/03. (\* indicates a location after rechlorination)

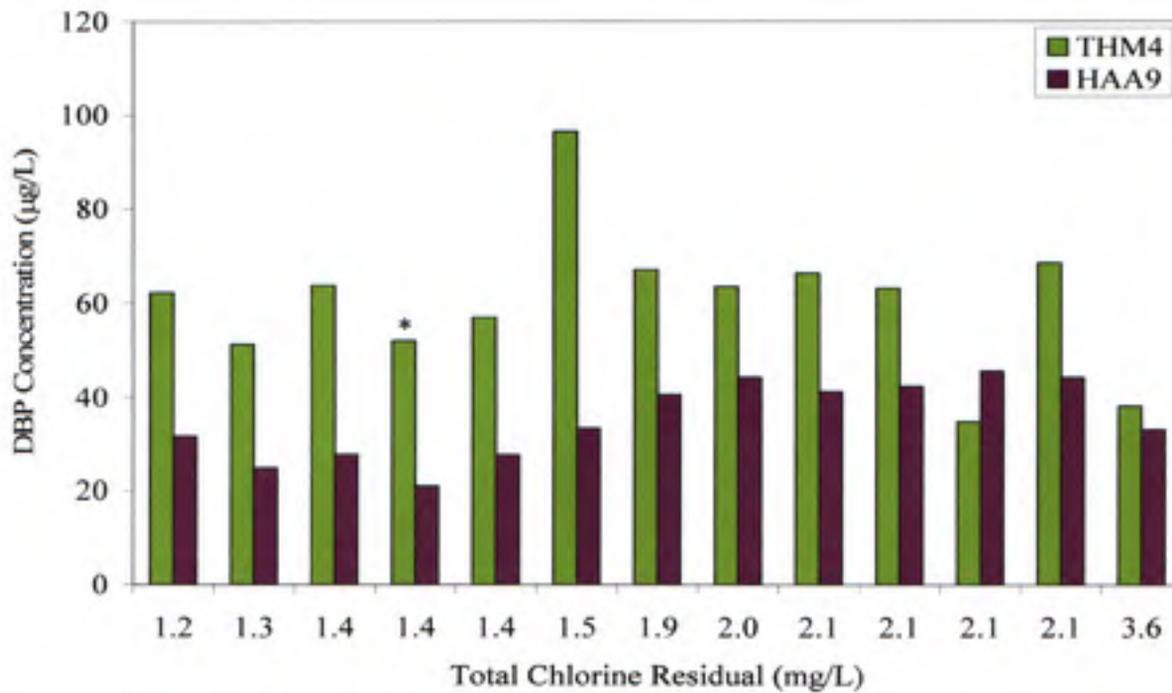


Figure B.16 THM4 and HAA9 versus total chlorine residual for Utility A for 2/25/03. (\* indicates a location after rechlorination)

Table B.17

pH, temperature and chlorine data for Utility A for 6/10/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
EP001	15.0	9.2	2.6	2.8
MR001	12.0	9.2	1.3	1.5
RD002	13.0	9.0	1.1	1.2
RD004	16.0	9.2	1.3	1.3
RD005	12.5	9.0	1.0	1.0
RD007	20.0	9.2	1.2	1.3
RD013	14.0	9.0	1.4	1.4
RD018	17.0	8.7	0.8	1.9
RD020	13.0	9.1	1.6	1.6
RD025	15.0	9.1	0.5	0.7
RD027	14.0	8.9	1.2	1.4
RD028	13.0	9.1	1.6	1.7
RD029	16.0	9.1	0.9	0.9

Table B.18

Organic carbon and microbiological data for Utility A for 6/10/03

Sample ID	AOC (mg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
EP001	550	2.13	0.045	8.0E+02
MR001				7.2E+02
RD002				1.2E+03
RD004				2.0E+03
RD005				1.6E+03
RD007				2.1E+03
RD013				8.9E+02
RD018				6.2E+02
RD020				1.6E+03
RD025				7.5E+02
RD027				3.8E+03
RD028				3.8E+03
RD029				1.4E+03

Table B.19

Trihalomethane (THM) data (in µg/L) for Utility A for 6/10/03

Sample ID	CHCl <sub>3</sub> *	CHBrCl <sub>2</sub> *	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	THM4
EP001	37	10	3	<1	50
MR001	71	22	9	<1	102
RD002	57	17	7	<1	80
RD004	66	21	9	<1	96
RD005	57	17	6	<1	80
RD007	47	15	6	<1	68
RD013	56	18	7	<1	81
RD018	50	16	7	<1	73
RD020	81	24	10	1	115
RD025	121	29	11	<1	161
RD027	85	23	9	<1	117
RD028	80	23	10	1	114
RD029	67	20	8	<1	95

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

Table B.20

Haloacetic acid (HAA) data (in µg/L) for Utility A for 6/10/03

Sample ID	ClAA*	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA*	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
EP001	5	<2	14	3	<2	4	4	<2	3	31
MR001	9	<2	15	4	2	3	4	<2	2	40
RD002	5	<2	15	4	<2	6	3	<2	2	36
RD004	7	<2	14	4	2	3	4	<2	2	36
RD005	6	<2	14	3	<2	4	3	<2	<2	31
RD007	7	<2	15	4	<2	6	4	<2	2	39
RD013	5	<2	14	4	<2	4	4	<2	<2	30
RD018	7	<2	13	4	<2	6	4	<2	2	36
RD020	5	<2	14	5	2	5	4	<2	2	38
RD025	5	<2	11	4	<2	6	4	<2	<2	29
RD027	6	<2	12	4	<2	6	4	<2	<2	32
RD028	5	<2	13	4	<2	4	4	<2	<2	30
RD029	7	<2	15	4	2	4	4	<2	2	37

\*Matrix spike data does not meet QA/QC requirements

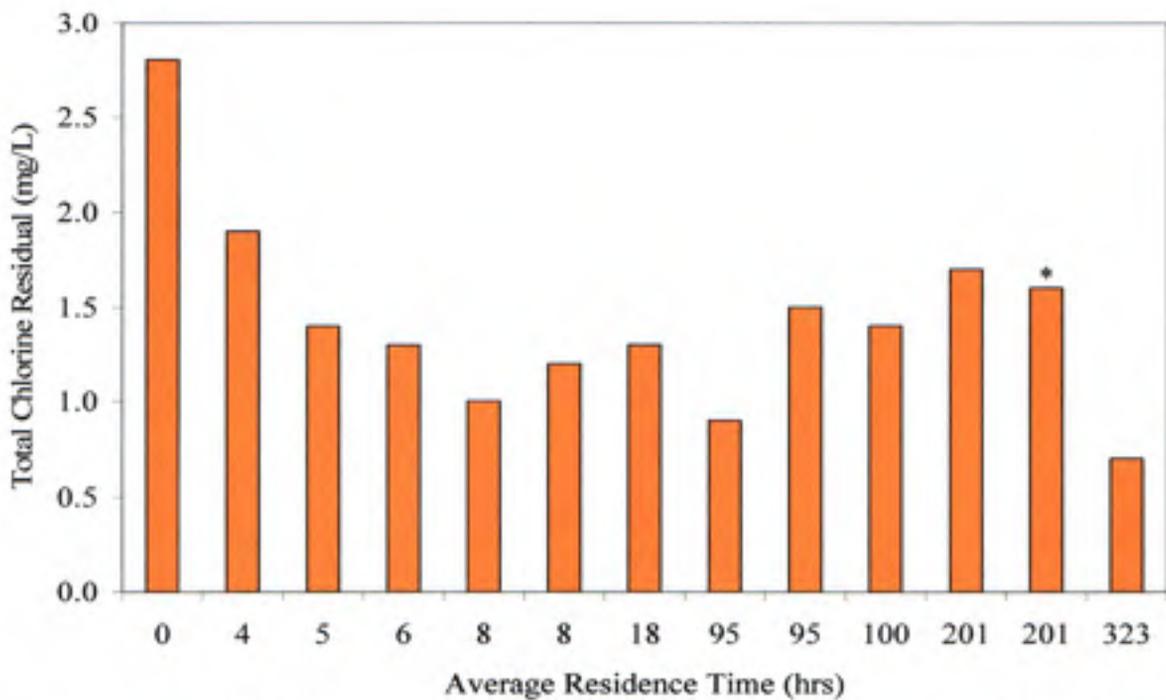


Figure B.17 Total chlorine residual versus average residence time for Utility A for 6/10/03. (\* indicates a location after rechlorination)

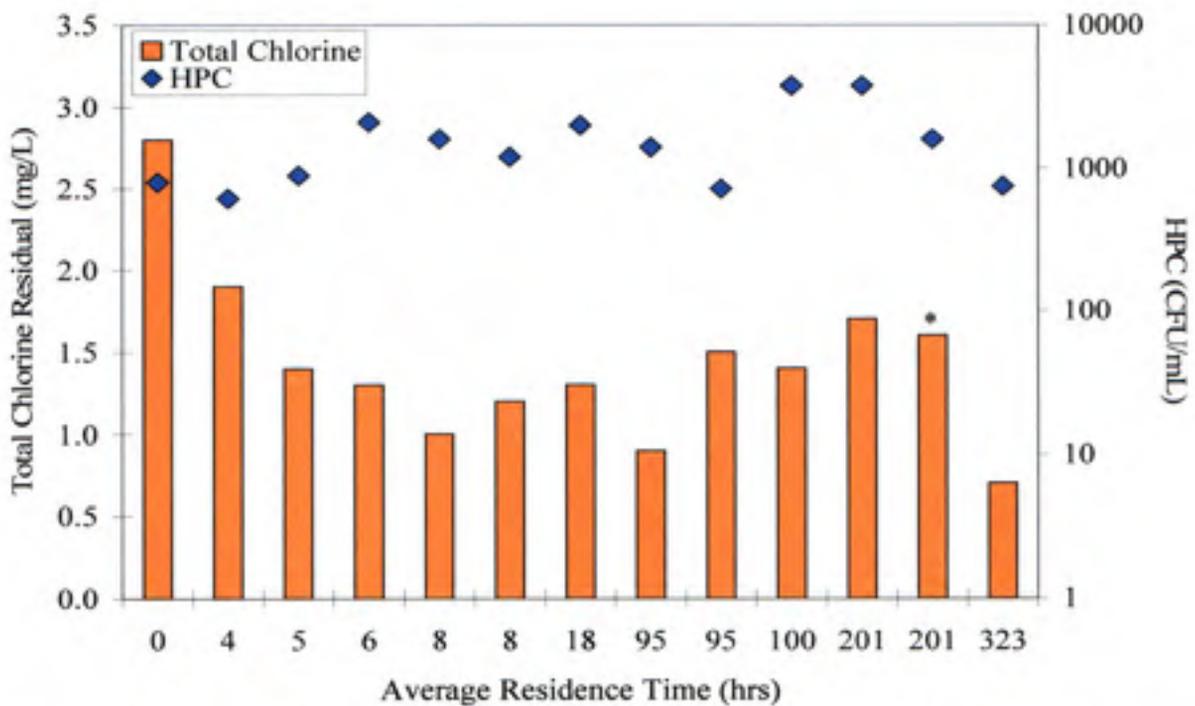


Figure B.18 Total chlorine residual and HPC versus average residence time for Utility A for 6/10/03. (\* indicates a location after rechlorination)

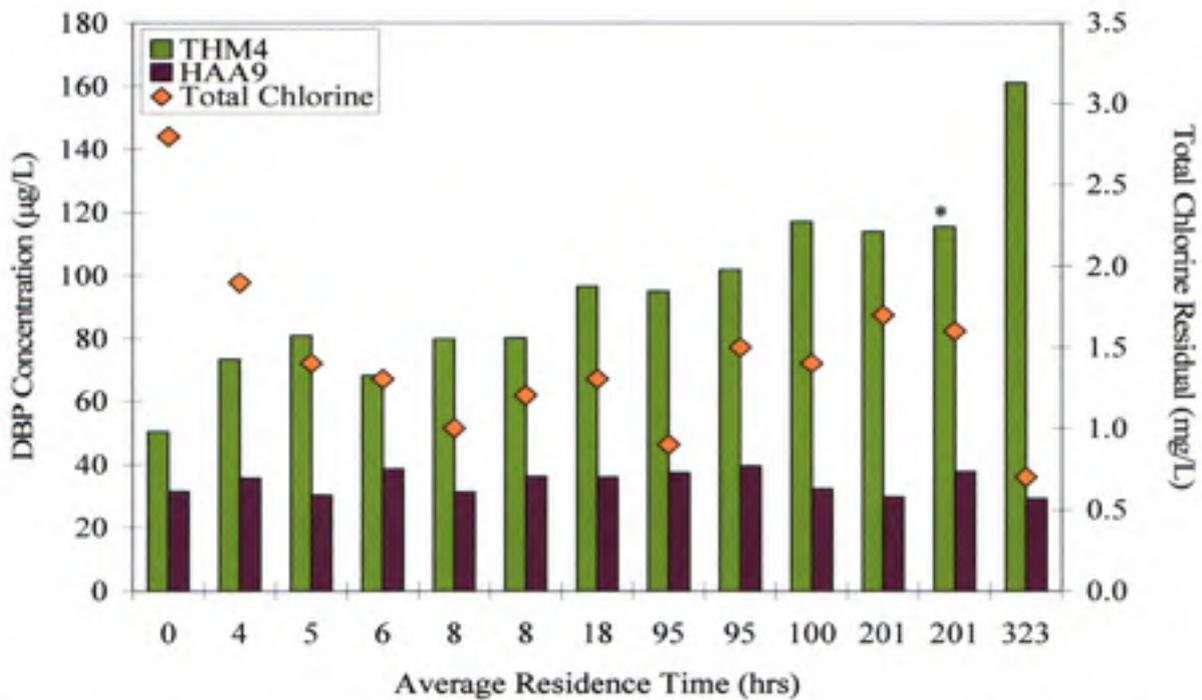


Figure B.19 THM4, HAA9 and total chlorine residual versus average residence time for Utility A for 6/10/03. (\* indicates a location after rechlorination)

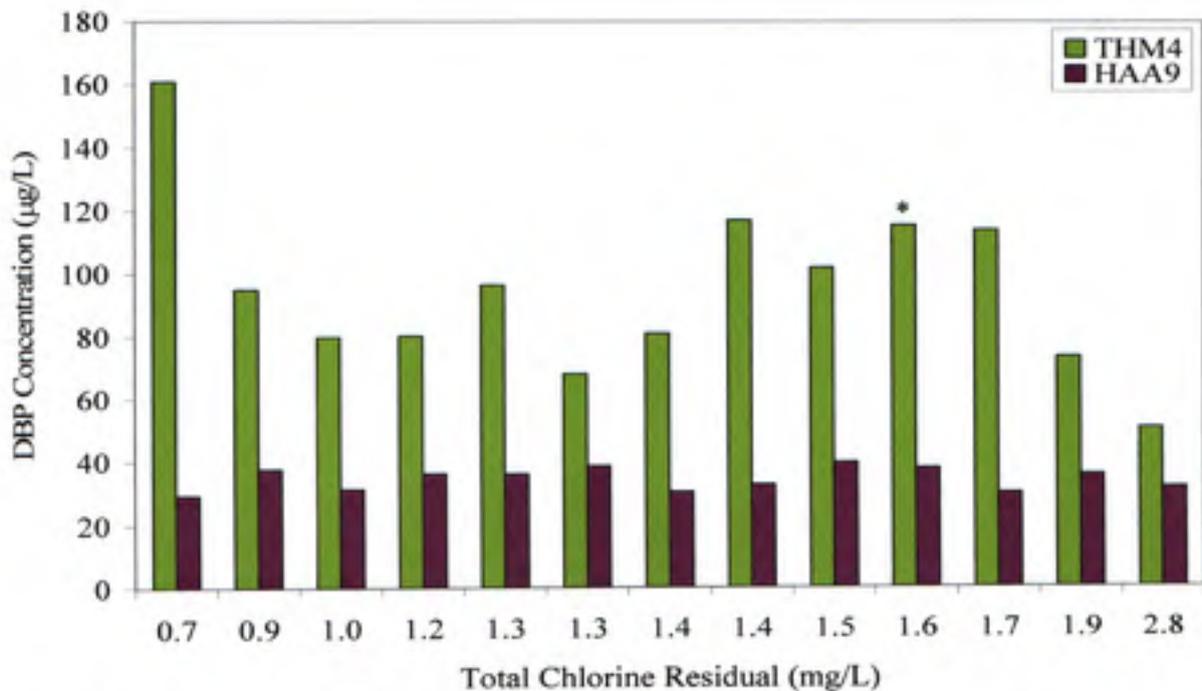


Figure B.20 THM4 and HAA9 versus total chlorine residual for Utility A for 6/10/03. (\* indicates a location after rechlorination)

Table B.21

pH, temperature and chlorine data for Utility A for 8/12/03

Sample ID	Temperature		Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
	(°C)	pH		
EP001	20.1	9.2	3.6	3.7
MR001	18.0	9.2	1.1	1.2
RD002	18.0	9.0	2.1	2.3
RD004	19.0	9.0	0.9	1.2
RD005	19.0	9.1	2.0	2.2
RD007	18.0	8.9	2.1	2.1
RD013	19.0	9.0	2.4	2.4
RD018	22.5	8.9	0.5	0.8
RD020	18.0	9.2	1.2	1.4
RD025	17.5	9.1	0.3	0.4
RD027	21.0	9.2	0.2	0.3
RD028	21.0	9.1	1.2	1.2
RD029	20.0	9.2	1.1	1.5

Table B.22

Organic carbon and microbiological data for Utility A for 8/12/03

Sample ID	AOC (mg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
EP001	513	2.46	0.033	1.0E+01
MR001				1.0E+01
RD002				NA
RD004				7.4E+02
RD005				2.4E+02
RD007				3.2E+02
RD013				2.0E+01
RD018				1.3E+02
RD020				5.4E+02
RD025				4.1E+02
RD027				2.8E+03
RD028				4.7E+02
RD029				2.0E+02

Table B.23

Trihalomethane (THM) data (in µg/L) for Utility A for 8/12/03

Sample ID	CHCl <sub>3</sub> *	CHBrCl <sub>2</sub> *	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	THM4
EP001	47	4	2	<1	54
MR001	147	23	6	<1	176
RD002	88	13	5	<1	106
RD004	131	21	6	<1	157
RD005	114	18	5	<1	137
RD007	79	11	5	<1	95
RD013	81	12	5	<1	97
RD018	138	20	5	<1	163
RD020	168	27	7	<1	202
RD025	226	34	10	<1	269
RD027	166	25	6	<1	197
RD028	167	25	7	<1	199
RD029	147	23	6	<1	176

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

Table B.24

Haloacetic acid (HAA) data (in µg/L) for Utility A for 8/12/03

Sample ID	ClAA*	BrAA	Cl <sub>2</sub> AA*	BrClAA*	Br <sub>2</sub> AA*	Cl <sub>3</sub> AA*	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
EP001	<2	<2	14	2	<2	3	3	2	4	28
MR001	3	<2	26	5	<2	6	4	3	6	53
RD002	3	<2	18	3	<2	4	4	<2	3	36
RD004	2	<2	23	4	<2	5	4	<2	3	42
RD005	2	<2	24	5	<2	5	5	3	14	58
RD007	2	<2	17	3	<2	4	4	<2	3	34
RD013	2	<2	19	3	<2	4	4	<2	8	40
RD018	**	**	**	**	**	**	**	**	**	**
RD020	<2	<2	8	<2	<2	7	4	<2	2	21
RD025	<2	<2	13	3	<2	10	5	<2	3	33
RD027	<2	<2	7	<2	<2	7	4	<2	15	33
RD028	<2	<2	9	2	<2	7	4	2	7	31
RD029	3	<2	26	5	<2	6	5	<2	3	48

\*Matrix spike data does not meet QA/QC requirements; all other QA/QC requirements were met

\*\* High internal standard

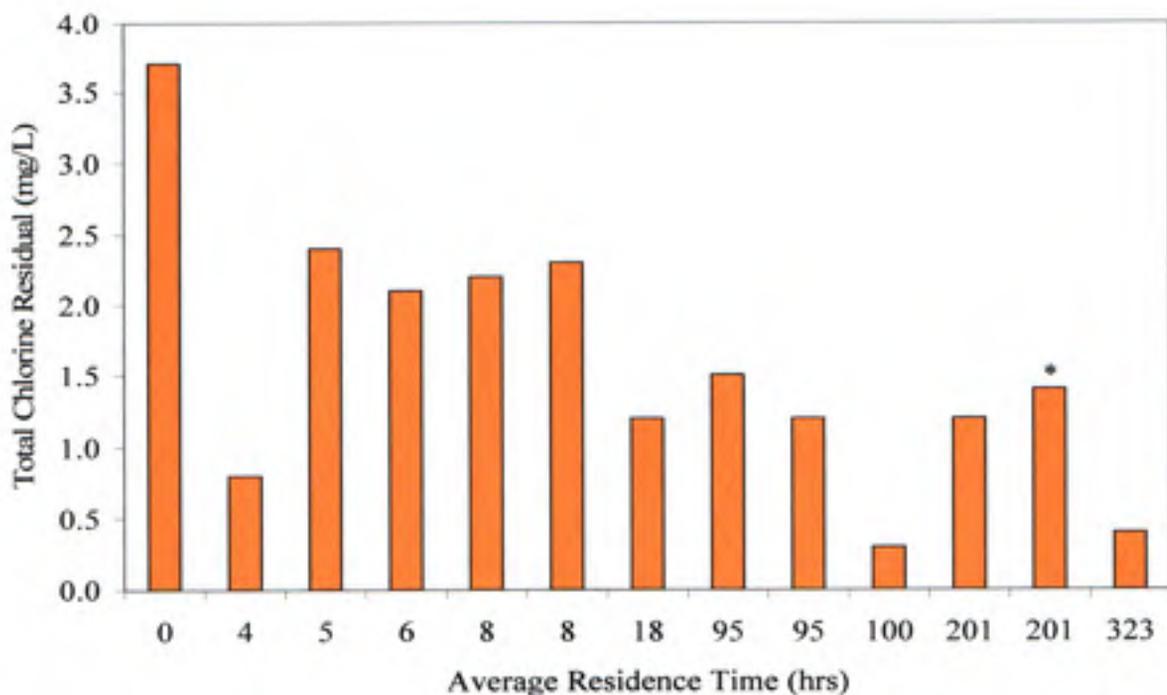


Figure B.21 Total chlorine residual versus average residence time for Utility A for 8/12/03. (\* indicates a location after rechlorination)

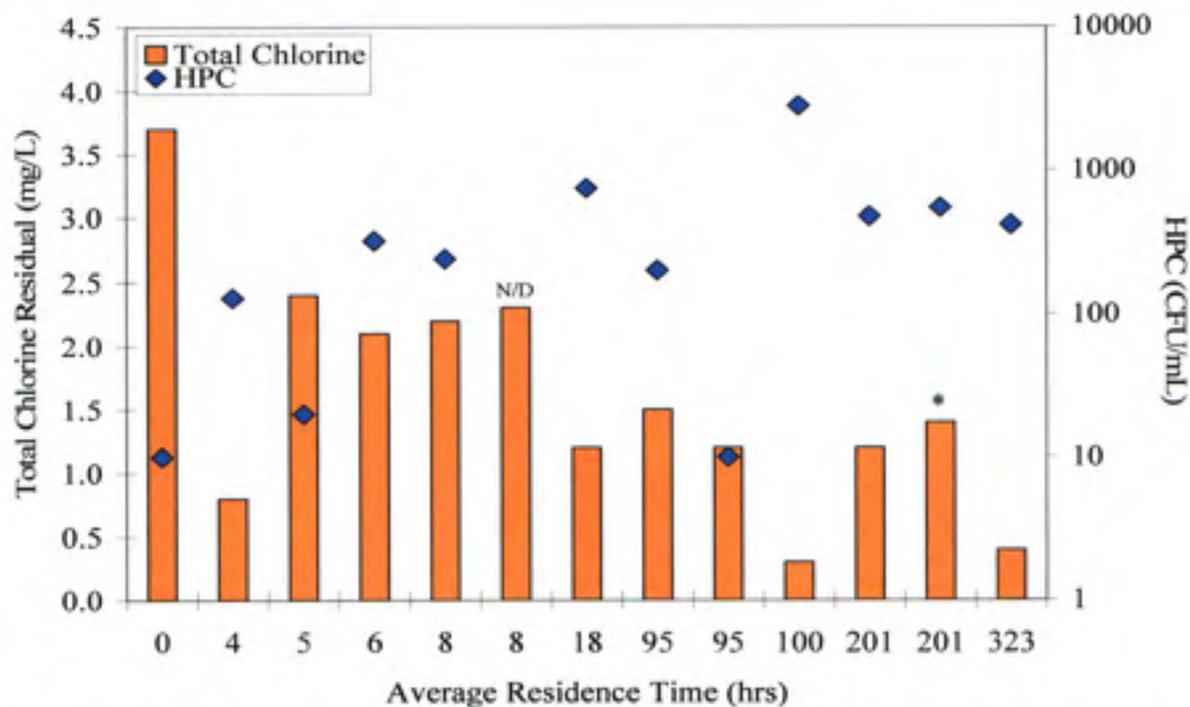


Figure B.22 Total chlorine residual and HPC versus average residence time for Utility A for 8/12/03. (\* indicates a location after rechlorination)

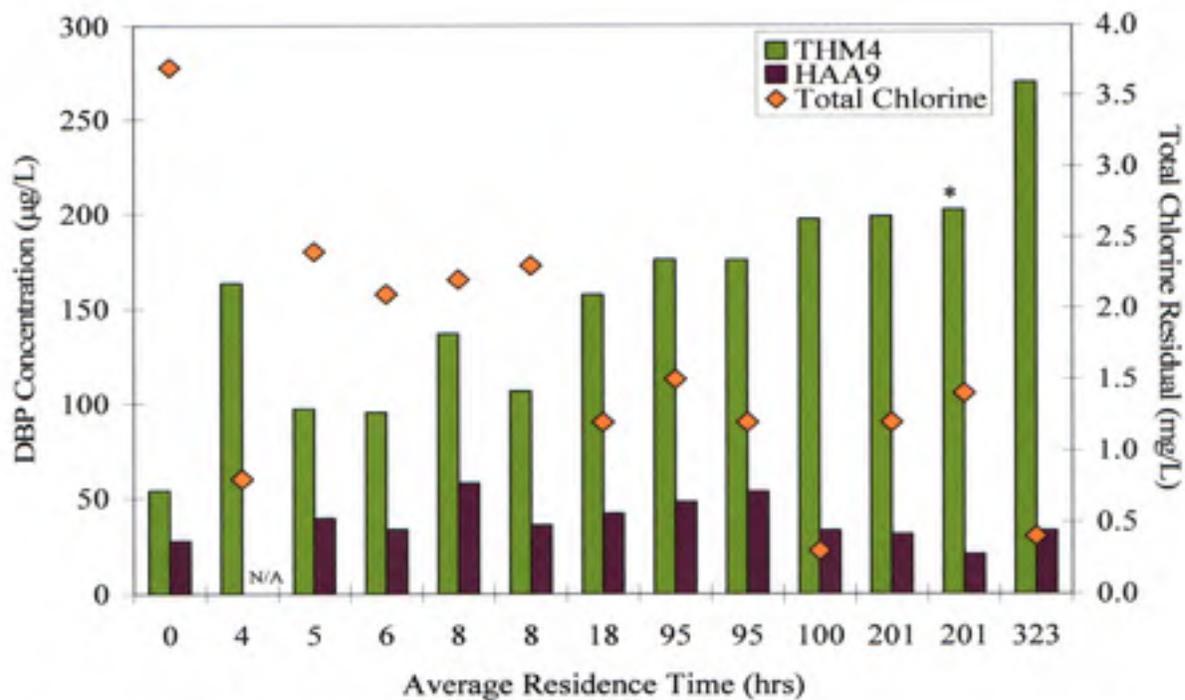


Figure B.23 THM4, HAA9 and total chlorine residual versus average residence time for Utility A for 8/12/03. (\* indicates a location after rechlorination)

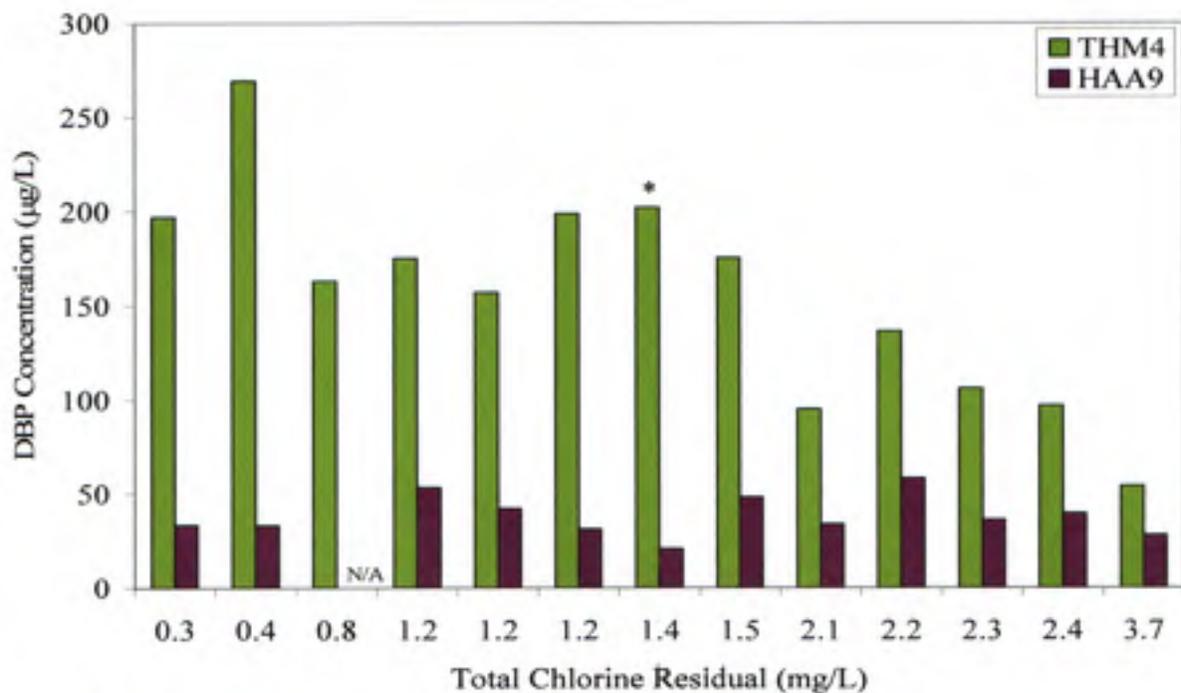


Figure B.24 THM4 and HAA9 versus total chlorine residual for Utility A for 8/12/03. (\* indicates a location after rechlorination)

**APPENDIX C**  
**Utility B**

Table C.1

pH, temperature and chlorine data for Utility B for 10/16/02

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
WTP	26	8.9	1.7	2.0
308	24	8.8	1.3	1.4
883	24	9.1	1.5	1.6
975	24	9.2	1.5	1.7
979	23	9.0	1.5	1.6
208	23	9.0	1.6	1.6
232	23	9.1	1.6	1.7
100	23	8.9	1.6	1.7
116	24	8.9	1.1	1.2
251	24	9.0	1.5	1.7
227	25	9.1	1.5	1.7
X-3	25	9.0	1.4	1.5
R-1	24	9.1	1.4	1.6
D-6	24	9.0	1.3	1.5
X-11	25	9.0	1.7	1.8

Table C.2

Organic carbon and microbiological data for Utility B for 10/16/02

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
WTP	855	1.68	0.022	NA
308		1.86	0.025	
883		2.28	0.025	<10
975		2.03	0.026	<10
979		2.16	0.027	<10
208		2.01	0.025	1.0E+01
232		1.85	0.028	2.0E+01
100		1.48	0.026	<10
116		1.98	0.024	<10
251		1.61	0.025	<10
227		1.79	0.024	
X-3		1.88	0.027	<10
R-1		1.53	0.026	<10
D-6		1.84	0.028	1.0E+01
X-11		1.79	0.027	<10

Table C.3

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility B for 10/16/02

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
WTP	26	15	8	2	51
308	26	15	7	2	50
883	26	14	7	2	49
975	32	16	8	2	58
979	37	17	8	2	64
208	58	20	9	2	89
232	38	17	8	2	65
100	41	19	9	2	71
116	34	15	8	2	59
251	39	18	9	2	68
227	56	20	9	2	87
X-3	30	17	8	2	57
R-1	30	17	8	2	57
D-6	32	16	8	2	58
X-11	28	15	8	2	53

Table C.4

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility B for 10/16/02

Sample ID	CIAA	BrAA	$\text{Cl}_2\text{AA}$	BrCIAA	$\text{Br}_2\text{AA}$	$\text{Cl}_3\text{AA}$	$\text{BrCl}_2\text{AA}$	$\text{Br}_2\text{CIAA}$	$\text{Br}_3\text{AA}$	HAA9
WTP	6	5	11	6	2	4	3	1	<1	38
308	7	7	14	8	2	6	3	2	<1	49
883	9	6	11	6	2	3	3	1	<1	41
975	8	6	15	9	2	7	4	2	<1	53
979	7	4	12	7	2	4	3	2	<1	41
208	7	2	26	11	3	7	4	2	<1	62
232	8	5	14	8	2	5	3	1	<1	46
100	8	3	12	6	2	4	3	1	<1	39
116	8	3	16	9	2	5	3	2	<1	48
251	7	3	14	8	2	4	3	2	<1	43
227	8	2	23	10	3	7	4	2	<1	59
X-3	7	7	15	9	3	7	5	2	<1	55
R-1	6	6	11	7	2	4	2	1	<1	39
D-6	2	5	12	7	2	4	2	1	<1	35
X-11	8	6	14	8	3	5	4	2	<1	50

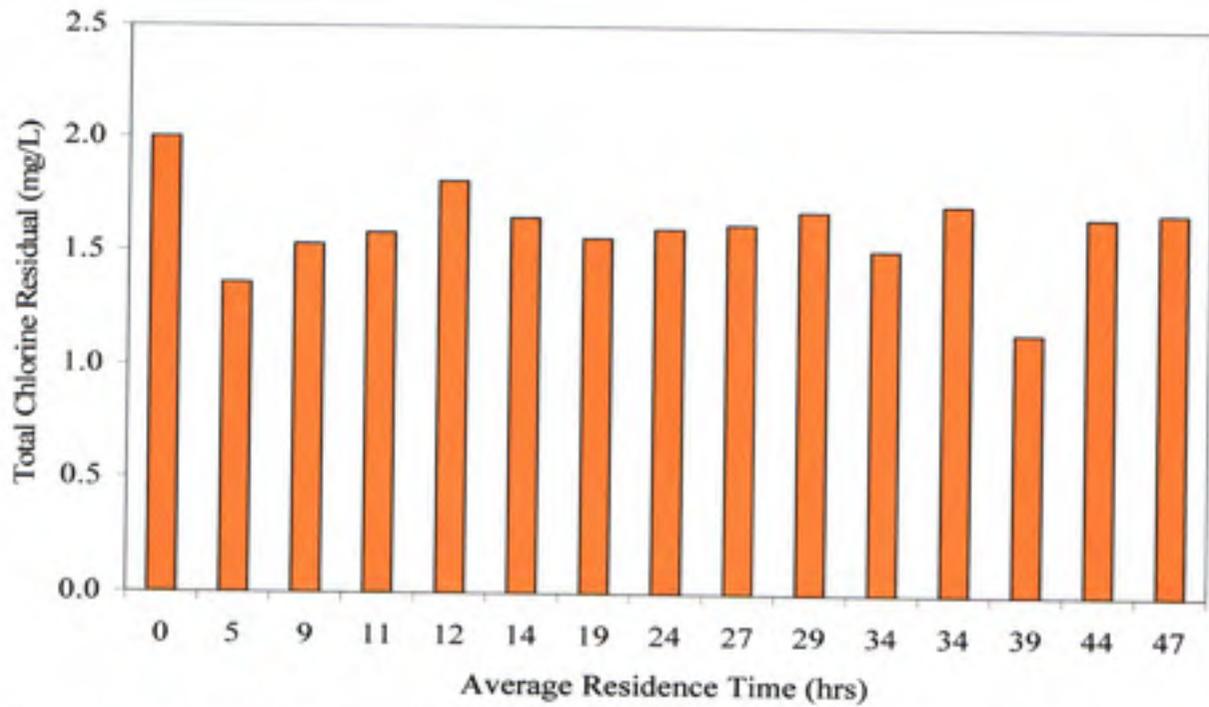


Figure C.1 Total chlorine residual versus average residence time for Utility B for 10/16/02

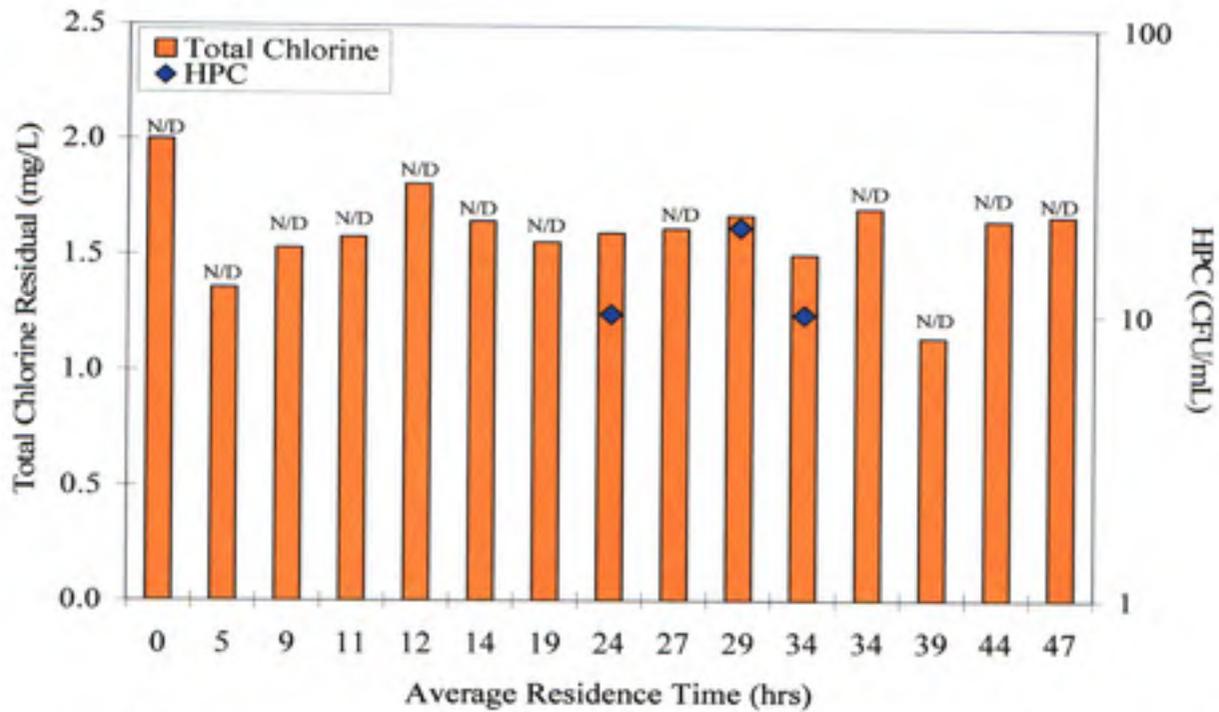


Figure C.2 Total chlorine residual and HPC versus average residence time for Utility B for 10/16/02

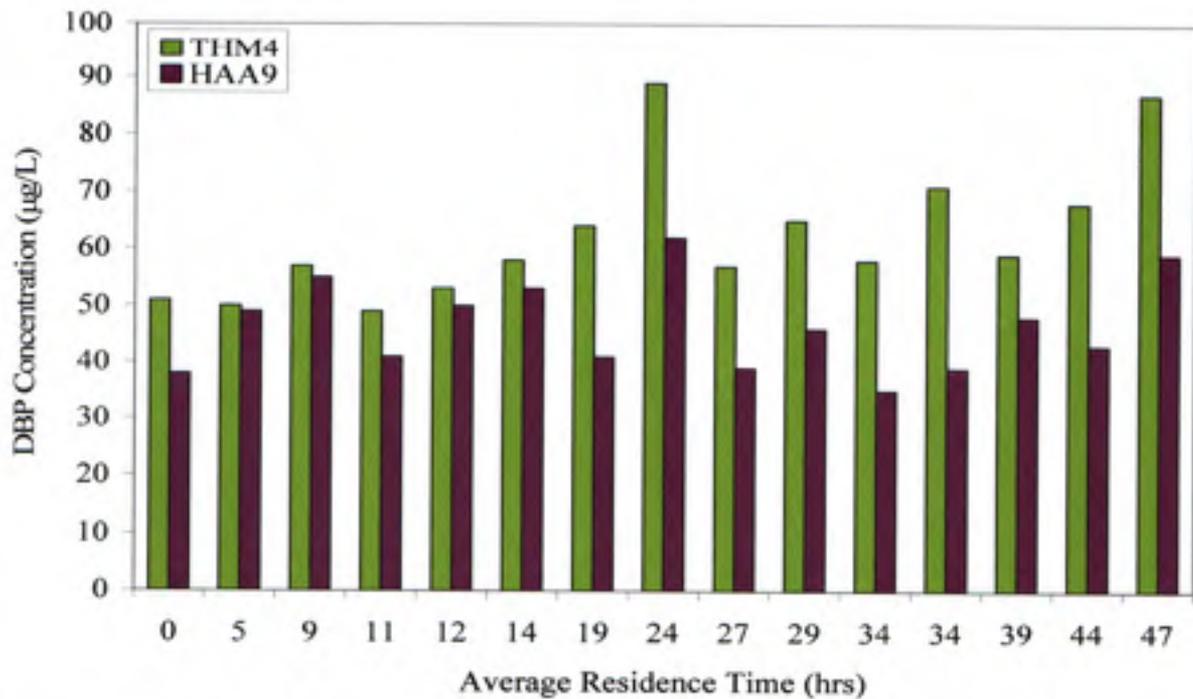


Figure C.3 THM4 and HAA9 versus average residence time for Utility B for 10/16/02

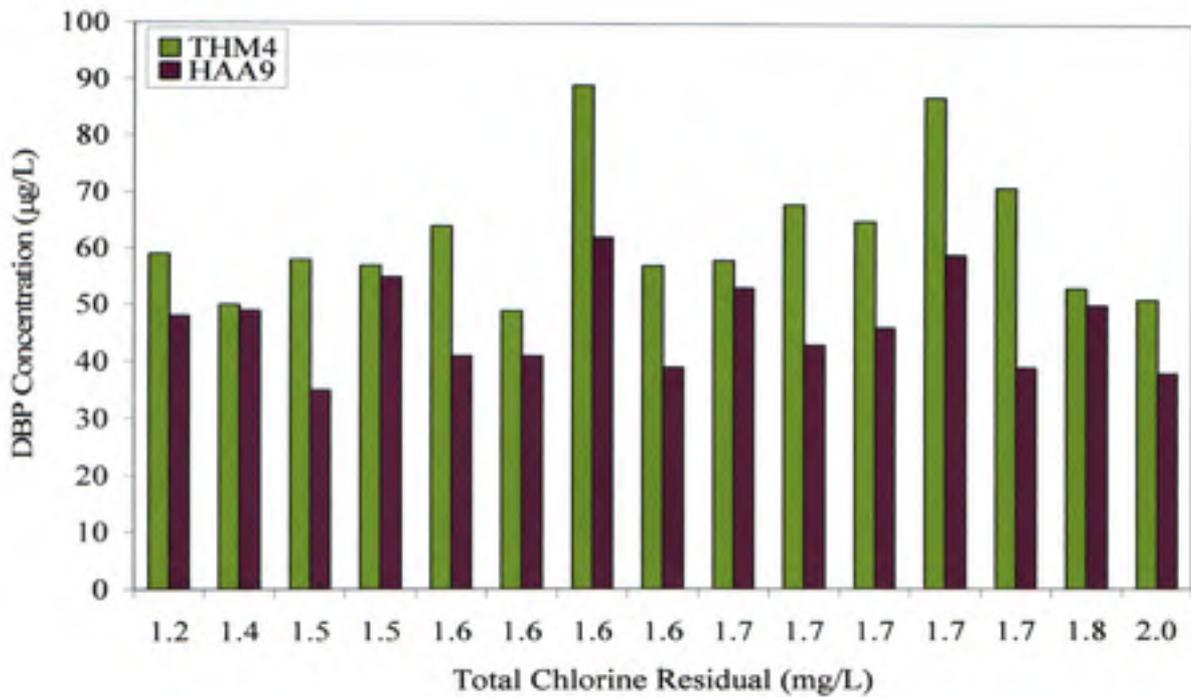


Figure C.4 THM4 and HAA9 versus total chlorine residual for Utility B for 10/16/02

Table C.5

pH, temperature and chlorine data for Utility B for 11/18/02

Sample ID	Temperature		Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
	(°C)	pH		
WTP	17	8.87	1.82	1.89
308	16	8.83	1.64	1.92
883	16	8.97	1.77	1.90
975	16	8.90	1.71	1.93
979	16	8.93	1.74	1.89
208	16	8.92	1.62	1.86
232	17	8.94	1.71	1.90
100	17	9.00	1.62	1.86
116	18	8.96	1.58	1.70
251	19	8.99	1.40	1.62
227	20	9.10	1.75	1.86
X-3	17	8.93	1.76	1.92
R-1	19	9.06	1.62	1.80
D-6	18	8.92	1.68	1.73
X-11	18	8.89	1.70	1.82

Table C.6

Organic carbon and microbiological data for Utility B for 11/18/02

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
WTP	274	1.70	0.029	9.0E+01
308		1.65	0.028	3.0E+01
883		2.13	0.029	2.0E+01
975		1.68	0.026	TNTC
979		1.85	0.029	5.0E+00
208		1.83	0.028	6.5E+01
232		1.78	0.029	5.0E+00
100		1.67	0.025	<10
116		1.83	0.028	<10
251		1.84	0.027	<10
227		1.61	0.028	<10
X-3		1.80	0.031	<10
R-1		1.71	0.028	1.0E+01
D-6		1.93	0.026	3.5E+01
X-11		2.03	0.030	1.2E+02

Table C.7

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility B for 11/18/02

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
WTP	30	14	5	<1	49
308	37	16	6	<1	59
883	32	15	5	<1	52
975	41	18	7	<1	66
979	34	16	6	<1	56
208	37	16	6	<1	59
232	38	17	6	<1	61
100	40	19	6	<1	65
116	39	16	6	<1	61
251	35	15	6	<1	56
227	58	20	8	<1	86
X-3	32	15	5	<1	52
R-1	38	17	7	<1	62
D-6	36	16	5	<1	57
X-11	39	17	7	<1	63

Table C.8

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility B for 11/18/02

Sample ID	CIAA	BrAA	$\text{Cl}_2\text{AA}$	BrCIAA	$\text{Br}_2\text{AA}$	$\text{Cl}_3\text{AA}$	$\text{BrCl}_2\text{AA}$	$\text{Br}_2\text{CIAA}$	$\text{Br}_3\text{AA}$	HAA9
WTP	6	7	19	9	2	13	5	1	<1	62
308	9	6	16	8	1	11	4	<1	<1	55
883	9	6	14	7	2	10	4	<1	<1	52
975	11	8	21	12	3	17	8	1	<1	81
979	11	9	21	11	2	17	7	1	<1	79
208	6	5	13	6	1	10	4	<1	<1	45
232	11	7	19	9	2	12	5	1	<1	66
100	11	6	19	10	3	14	6	1	<1	70
116	13	9	29	16	4	25	12	2	1	111
251	13	7	19	10	2	14	5	1	<1	71
227	8	3	18	9	2	10	4	1	<1	55
X-3	8	6	14	7	1	9	4	<1	<1	49
R-1	17	6	17	9	2	13	5	1	<1	70
D-6	12	6	15	8	1	10	4	<1	<1	56
X-11	13	7	21	11	3	16	7	1	<1	79

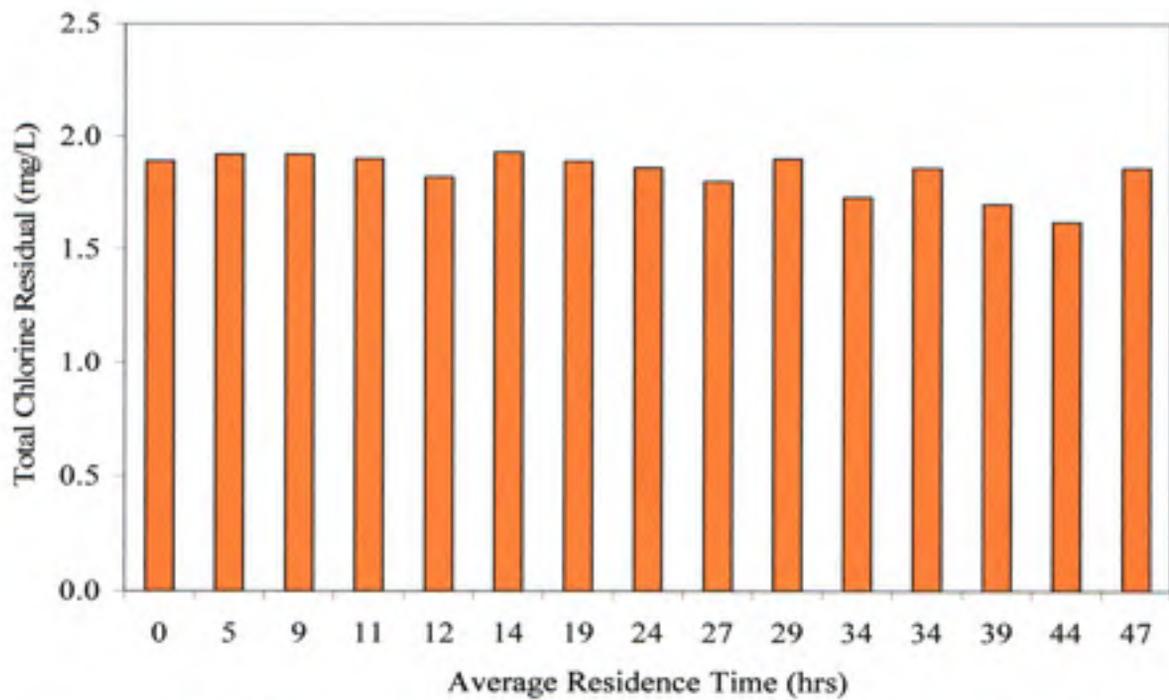


Figure C.5 Total chlorine residual versus average residence time for Utility B for 11/18/02

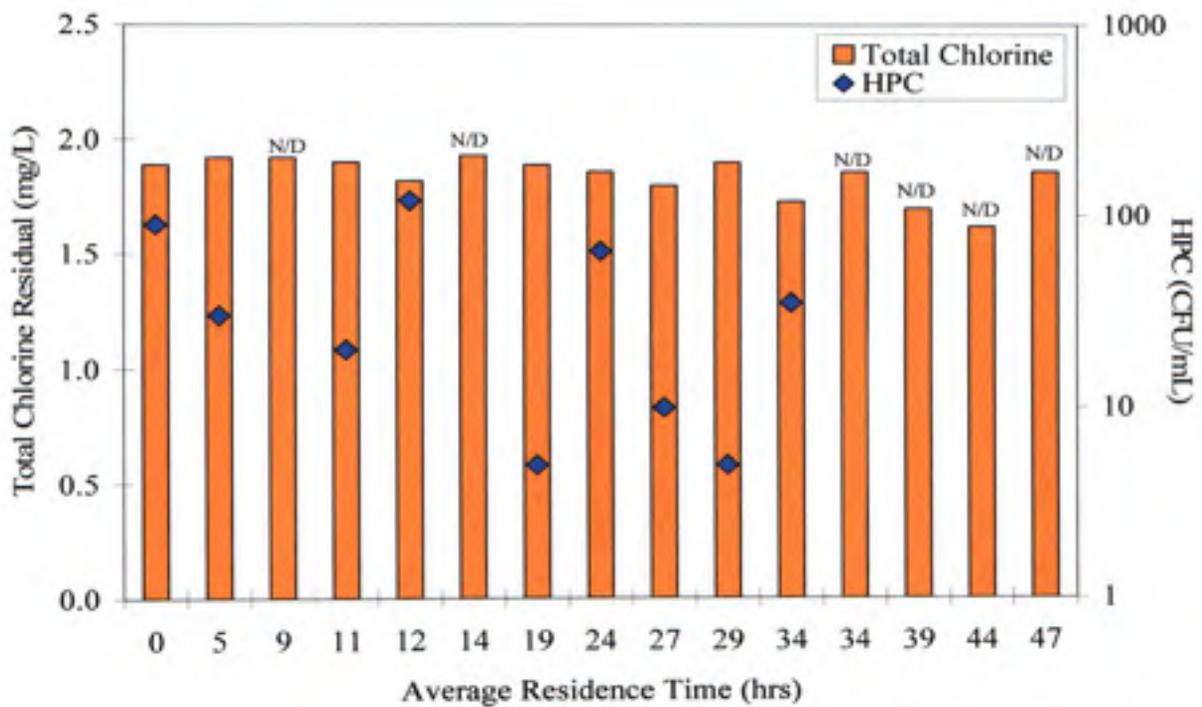


Figure C.6 Total chlorine residual and HPC versus average residence time for Utility B for 11/18/02

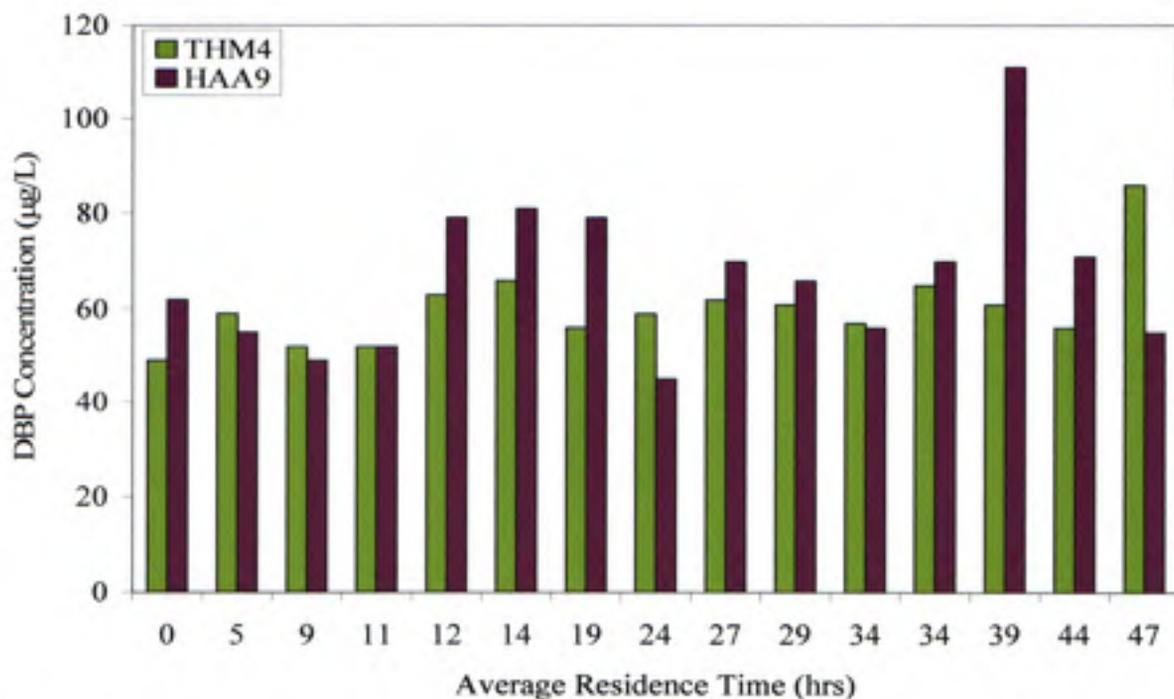


Figure C.7 THM4 and HAA9 versus average residence time for Utility B for 11/18/02

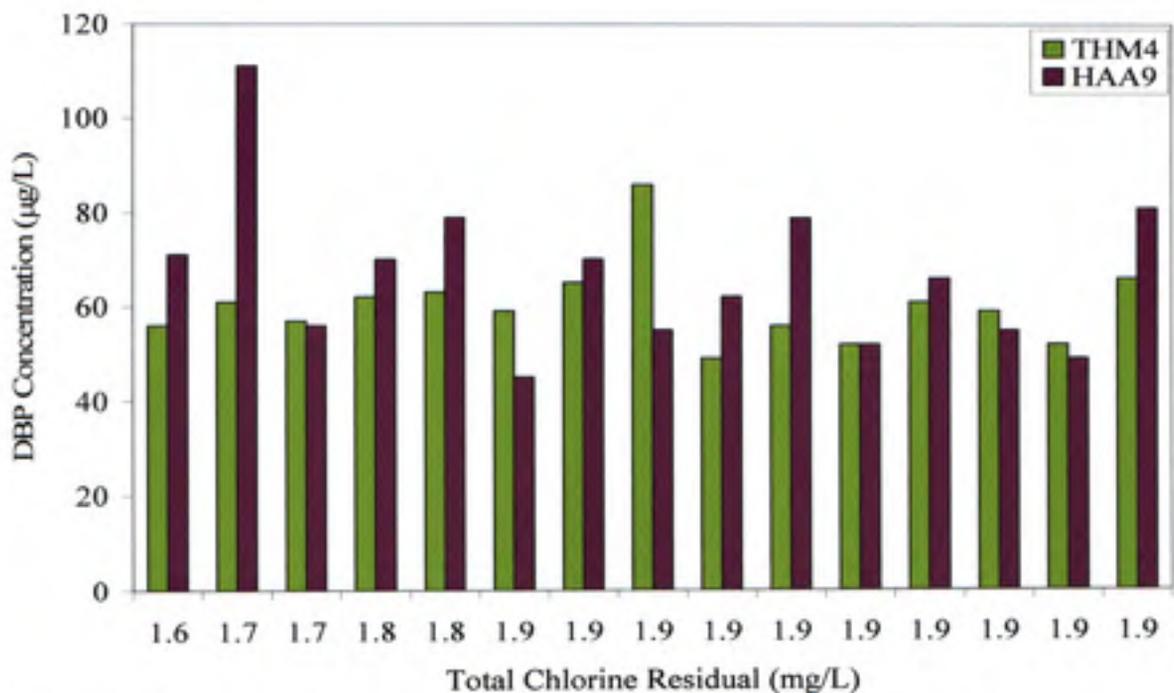


Figure C.8 THM4 and HAA9 versus total chlorine residual for Utility B for 11/18/02

Table C.9

pH, temperature and chlorine data for Utility B for 1/07/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
WTP	11	9.10	1.71	2.03
308	9	8.77	1.80	1.89
883	8	8.78	1.59	1.67
975	9	8.77	1.58	1.70
979	N/S	N/S	N/S	N/S
208	8	8.72	1.51	1.56
232	8	8.74	1.45	1.51
100	8	8.78	1.60	1.67
116	9	8.81	1.33	1.43
251	8	8.80	1.52	1.60
227	9	8.70	1.23	1.30
X-3	10	8.76	1.76	1.88
R-1	9	8.78	1.54	1.60
D-6	N/S	N/S	N/S	N/S
X-11	9	8.82	1.61	1.67

Table C.10

Organic carbon and microbiological data for Utility B for 1/07/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
WTP	127	1.47	0.020	5.0E+00
308		2.41	0.026	5.0E+00
883		1.72	0.024	6.5E+01
975		2.53	0.027	<10
979		N/S	N/S	2.6E+02
208		2.59	0.029	5.0E+00
232		2.20	0.027	5.0E+00
100		2.34	0.026	7.0E+01
116		1.70	0.022	3.7E+02
251		1.67	0.024	<10
227		1.62	0.021	4.0E+01
X-3		7.18	0.044	<10
R-1		2.52	0.030	<10
D-6		N/S	N/S	3.2E+02
X-11		2.31	0.033	2.0E+01

Table C.11

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility B for 1/07/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
WTP	25	11	3	<1	39
308	27	11	3	<1	41
883	30	11	3	<1	44
975	30	11	3	<1	44
979	N/S	N/S	N/S	N/S	N/S
208	34	12	4	<1	50
232	33	12	3	<1	48
100	35	12	3	<1	50
116	45	14	3	<1	62
251	33	12	4	<1	49
227	51	14	4	<1	69
X-3	23	10	3	<1	36
R-1	34	13	4	<1	51
D-6	N/S	N/S	N/S	N/S	N/S
X-11	48	15	4	<1	67

Table C.12

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility B for 1/07/03

Sample ID	ClAA	BrAA	$\text{Cl}_2\text{AA}$	BrClAA	$\text{Br}_2\text{AA}$	$\text{Cl}_3\text{AA}$	$\text{BrCl}_2\text{AA}$	$\text{Br}_2\text{ClAA}$	$\text{Br}_3\text{AA}$	HAA9
WTP	<2	3	13	4	1	8	3	1	<1	33
308	<2	4	12	4	1	7	3	1	<1	32
883	<2	4	16	4	1	8	3	1	<1	37
975	2	4	16	4	1	8	3	1	<1	39
979	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
208	2	4	16	5	2	9	4	1	<1	43
232	2	3	15	4	1	8	3	1	<1	37
100	<2	3	18	5	1	9	3	1	<1	40
116	<2	3	24	5	2	13	4	1	1	53
251	2	4	17	4	1	8	3	1	<1	40
227	3	3	25	5	2	13	4	1	<1	56
X-3	2	2	15	3	1	7	3	<1	<1	33
R-1	2	3	13	4	1	7	3	1	<1	34
D-6	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
X-11	3	3	28	6	2	12	4	1	<1	59

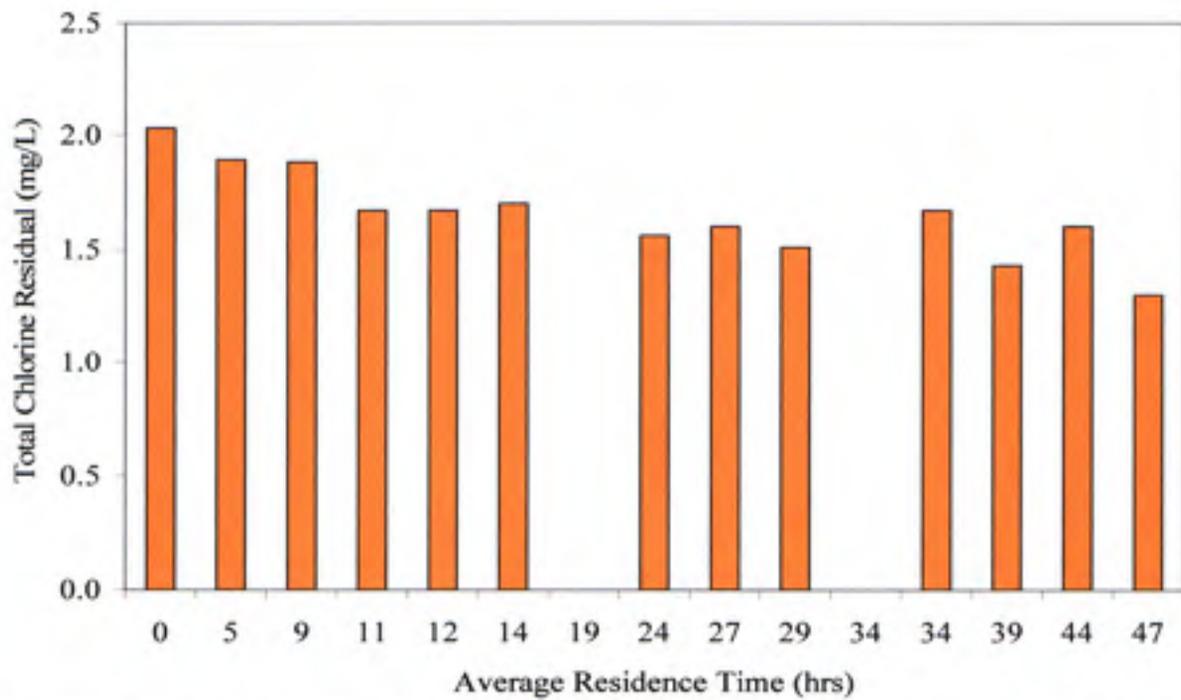


Figure C.9 Total chlorine residual versus average residence time for Utility B for 1/07/03

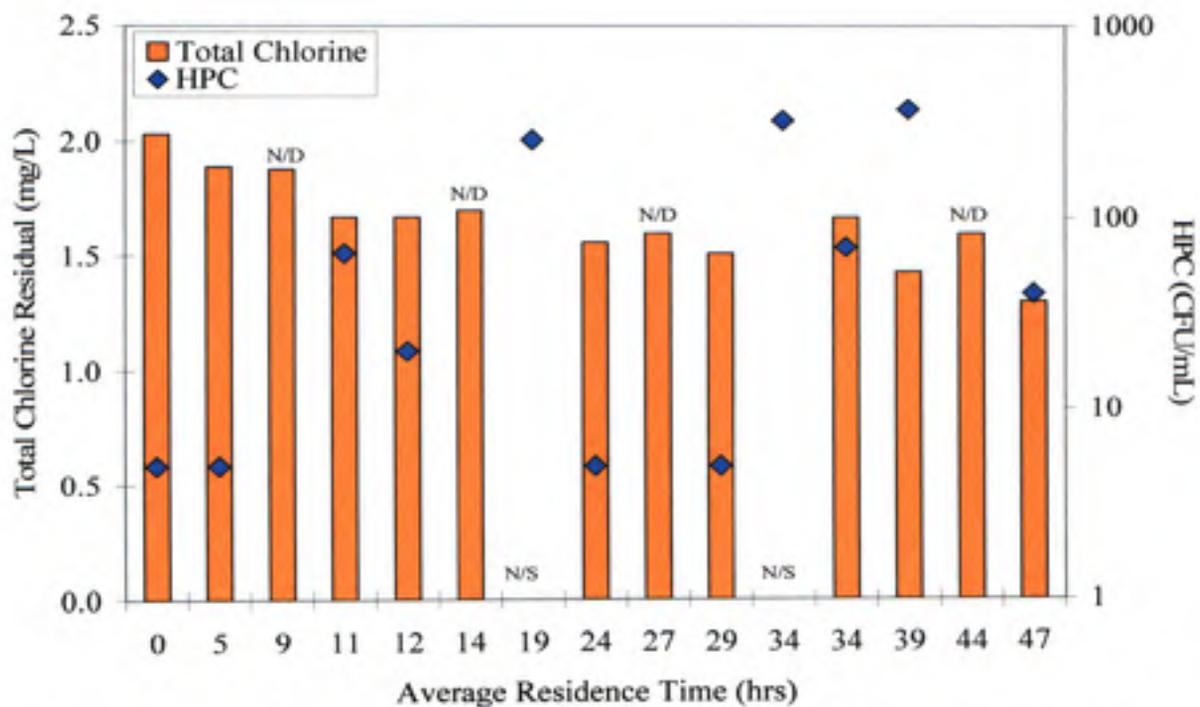


Figure C.10 Total chlorine residual and HPC versus average residence time for Utility B for 1/07/03

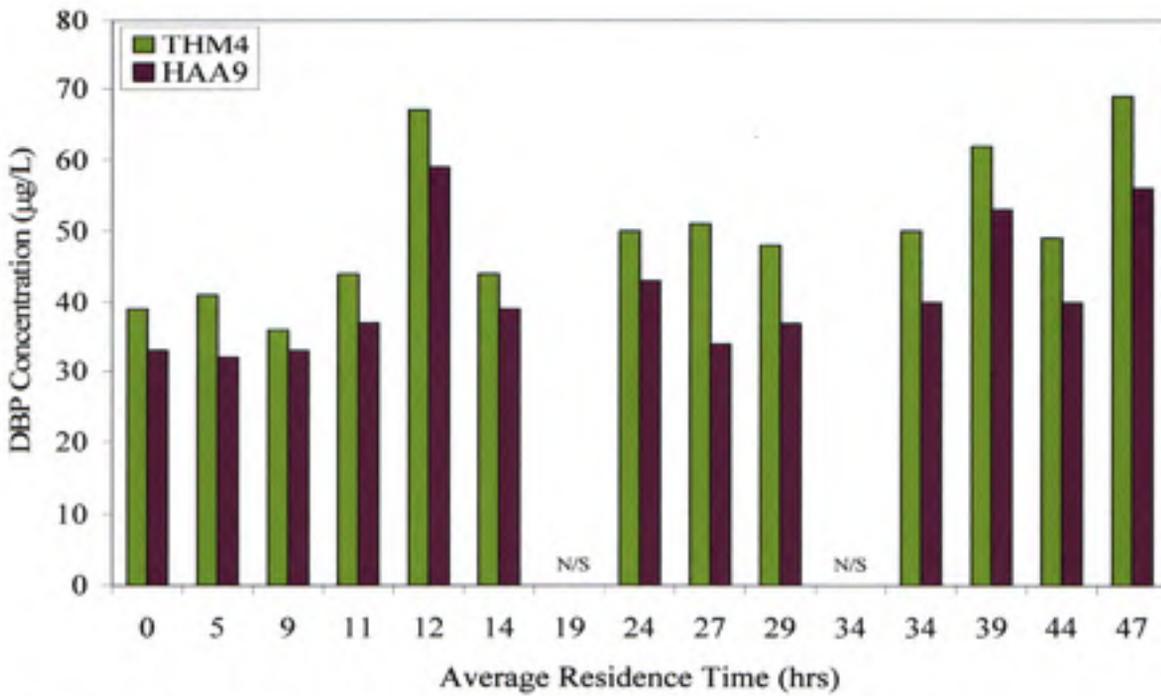


Figure C.11 THM4 and HAA9 versus average residence time for Utility B for 1/07/03

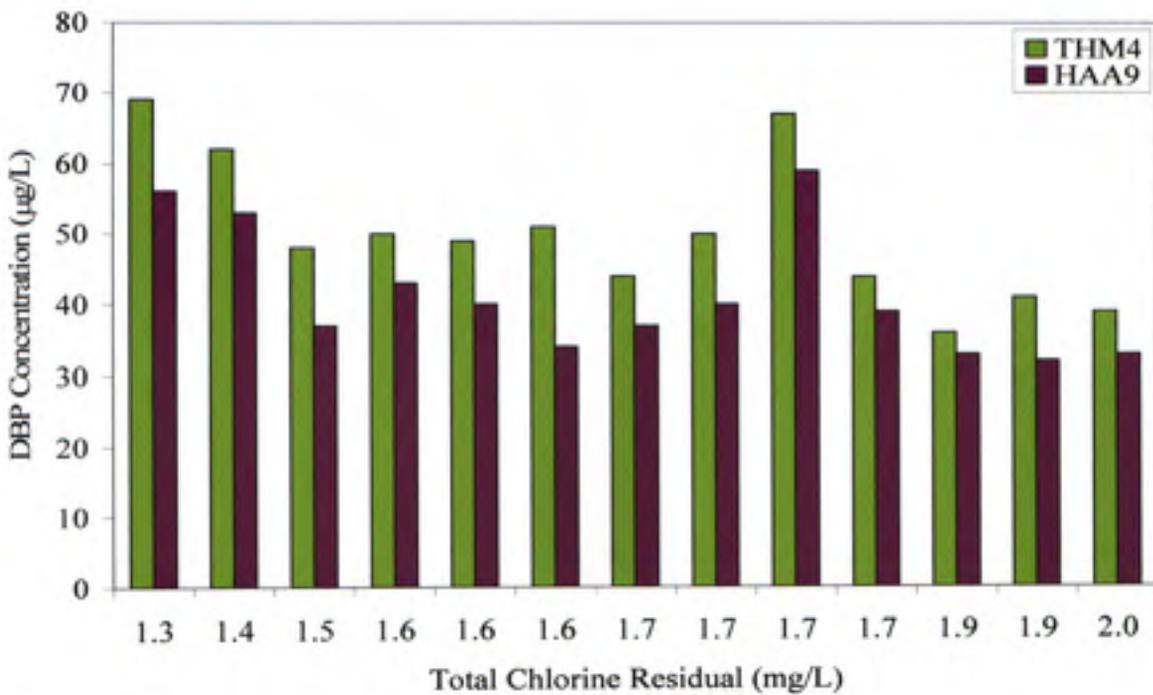


Figure C.12 THM4 and HAA9 versus total chlorine residual for Utility B for 1/07/03

Table C.13

pH, temperature and chlorine data for Utility B for 2/25/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
WTP	12	8.90	1.95	2.32
308	12	8.86	1.84	1.98
883	12	8.82	1.88	1.97
975	11	8.84	1.84	1.96
979	12	8.86	1.83	1.93
208	12	8.84	1.91	2.00
232	13	8.86	1.9	1.99
100	13	8.92	1.86	1.96
116	13	9.02	1.73	1.83
251	13	8.91	1.87	1.97
227	12	9.06	1.47	1.60
X-3	12	8.90	1.67	1.76
R-1	13	8.92	1.54	1.66
D-6	12	8.82	1.91	2.00
X-11	13	8.87	1.88	1.90

Table C.14

Organic carbon and microbiological data for Utility B for 2/25/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
WTP	278	1.56	0.023	<10
308		1.54	0.026	1.0E+01
883		1.56	0.026	2.2E+04
975		1.49	0.026	5.0E+00
979		N/S	N/S	5.0E+00
208		1.52	0.027	<10
232		1.58	0.029	<10
100		1.52	0.026	<10
116		1.63	0.024	4.0E+01
251		1.54	0.026	5.0E+00
227		1.69	0.027	2.0E+01
X-3		1.54	0.026	1.5E+01
R-1		1.56	0.028	1.0E+01
D-6		N/S	N/S	<10
X-11		1.48	0.026	2.0E+01

Table C.15

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility B for 2/25/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
WTP	34	11	3	<1	48
308	33	10	3	<1	46
883	36	11	3	<1	50
975	38	11	3	<1	52
979	N/S	N/S	N/S	N/S	N/S
208	38	11	3	<1	52
232	39	11	3	<1	53
100	40	12	3	<1	55
116	46	11	3	<1	60
251	39	11	3	<1	53
227	44	12	3	<1	59
X-3	37	11	3	<1	51
R-1	37	10	3	<1	50
D-6	N/S	N/S	N/S	N/S	N/S
X-11	37	11	3	<1	51

Table C.16

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility B for 2/25/03

Sample ID	ClAA	BrAA	$\text{Cl}_2\text{AA}$	BrClAA	$\text{Br}_2\text{AA}$	$\text{Cl}_3\text{AA}$	Br $\text{Cl}_2\text{AA}$	Br $_2\text{ClAA}$	Br $_3\text{AA}$	HAA9
WTP	<2	4	20	14	6	4	1	1	<1	50
308	5	3	18	9	5	3	2	<1	<1	45
883	2	3	19	9	4	3	2	<1	<1	42
975	6	4	20	12	5	4	2	1	<1	54
979	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
208	<2	3	18	9	5	3	2	<1	<1	40
232	<2	3	18	9	5	3	2	<1	<1	40
100	<2	3	19	11	5	3	2	<1	<1	43
116	<2	4	24	16	7	4	2	1	<1	58
251	2	3	18	11	5	3	2	<1	<1	44
227	<2	3	16	10	4	3	1	<1	<1	37
X-3	4	3	18	10	5	3	2	1	<1	46
R-1	2	4	19	10	5	3	2	<1	<1	45
D-6	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
X-11	<2	3	18	11	5	4	1	1	<1	43

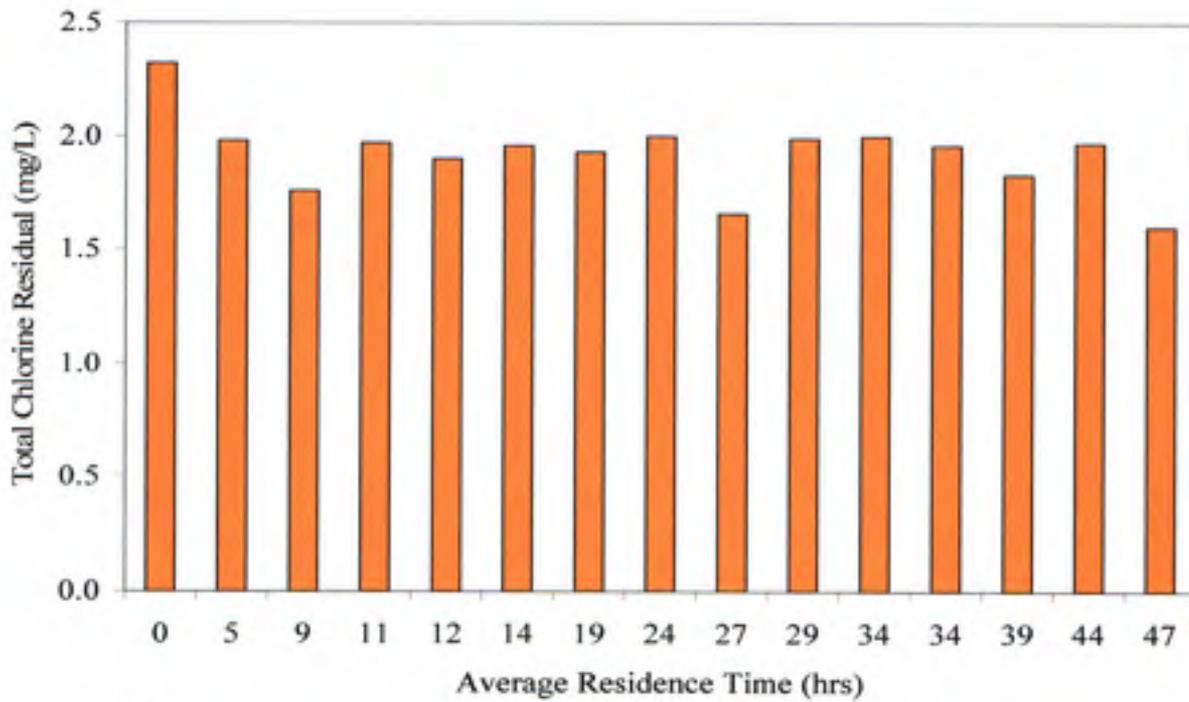


Figure C.13 Total chlorine residual versus average residence time for Utility B for 2/25/03

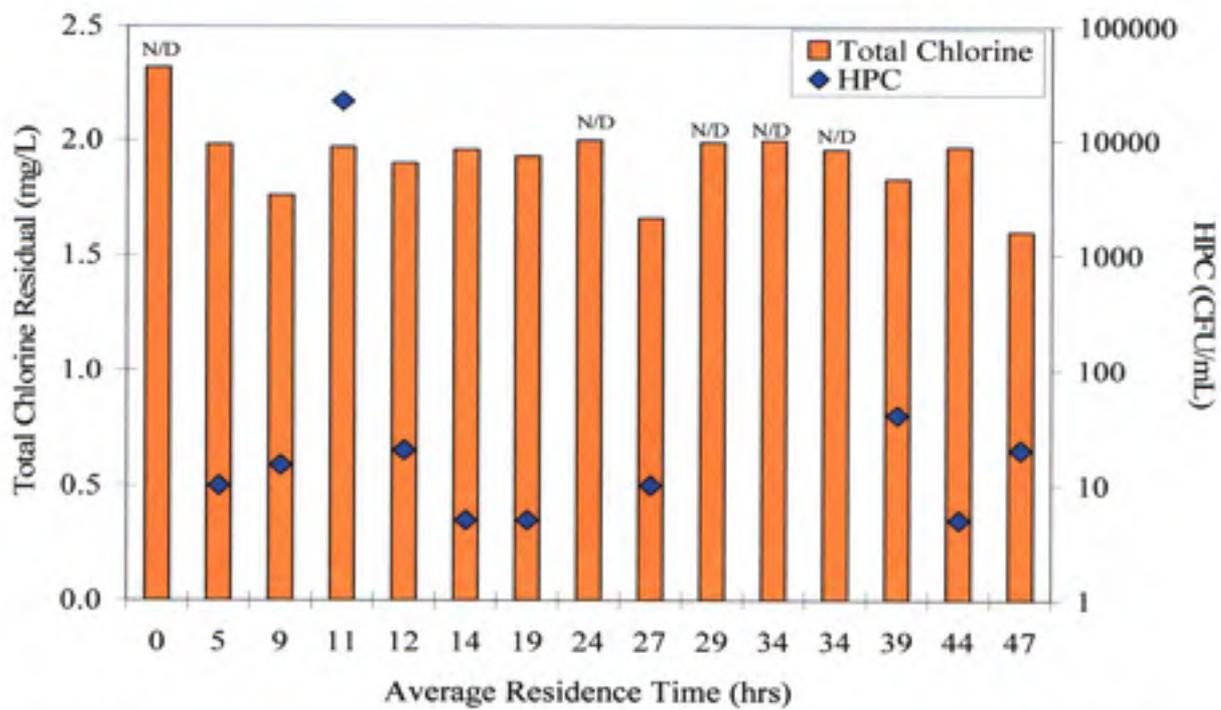


Figure C.14 Total chlorine residual and HPC versus average residence time for Utility B for 2/25/03

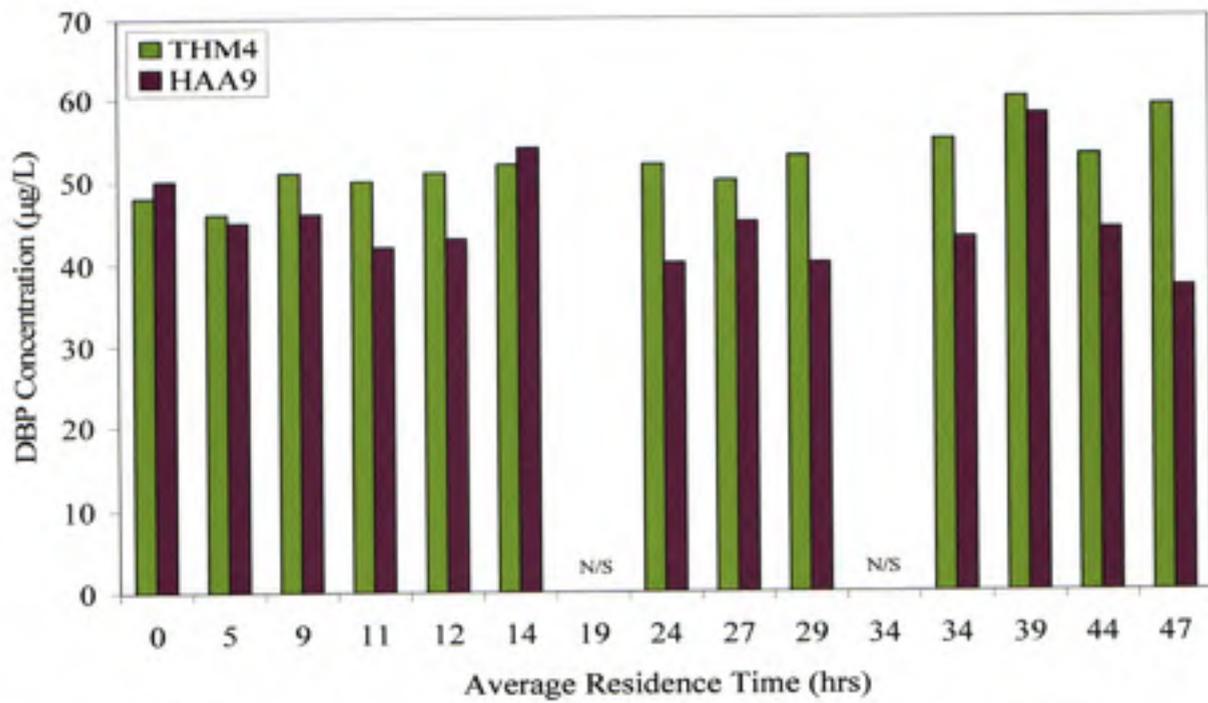


Figure C.15 THM4 and HAA9 versus average residence time for Utility B for 2/25/03

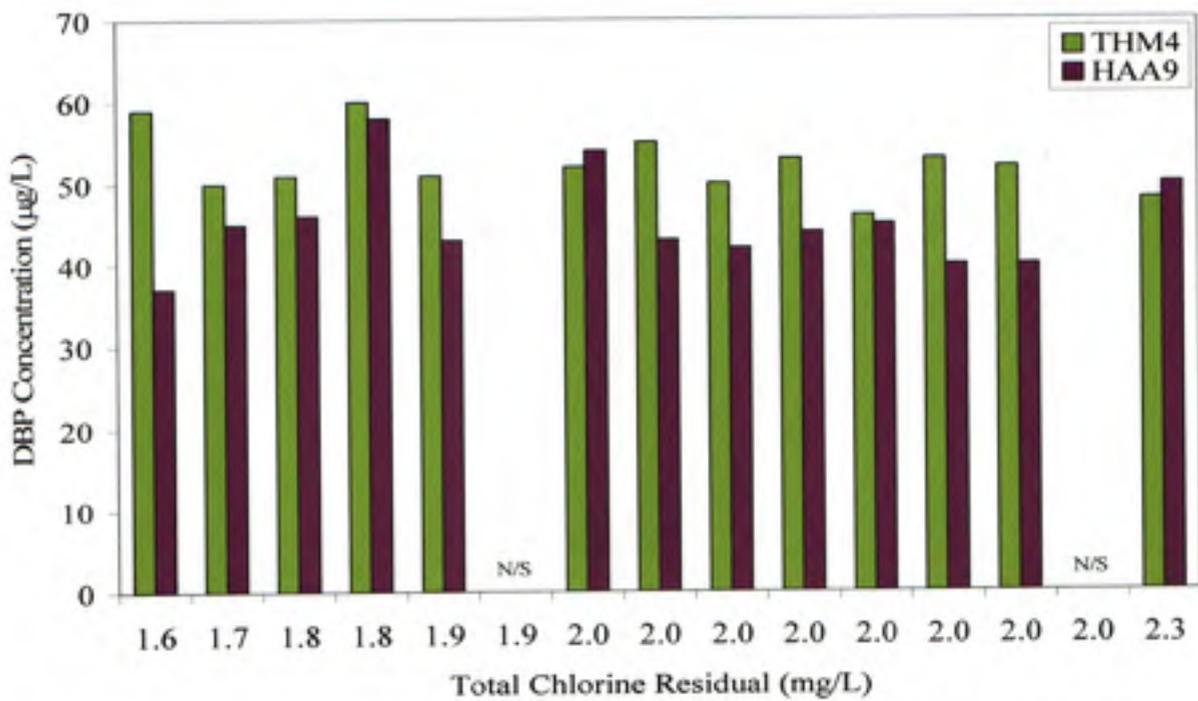


Figure C.16 THM4 and HAA9 versus total chlorine residual for Utility B for 2/25/03

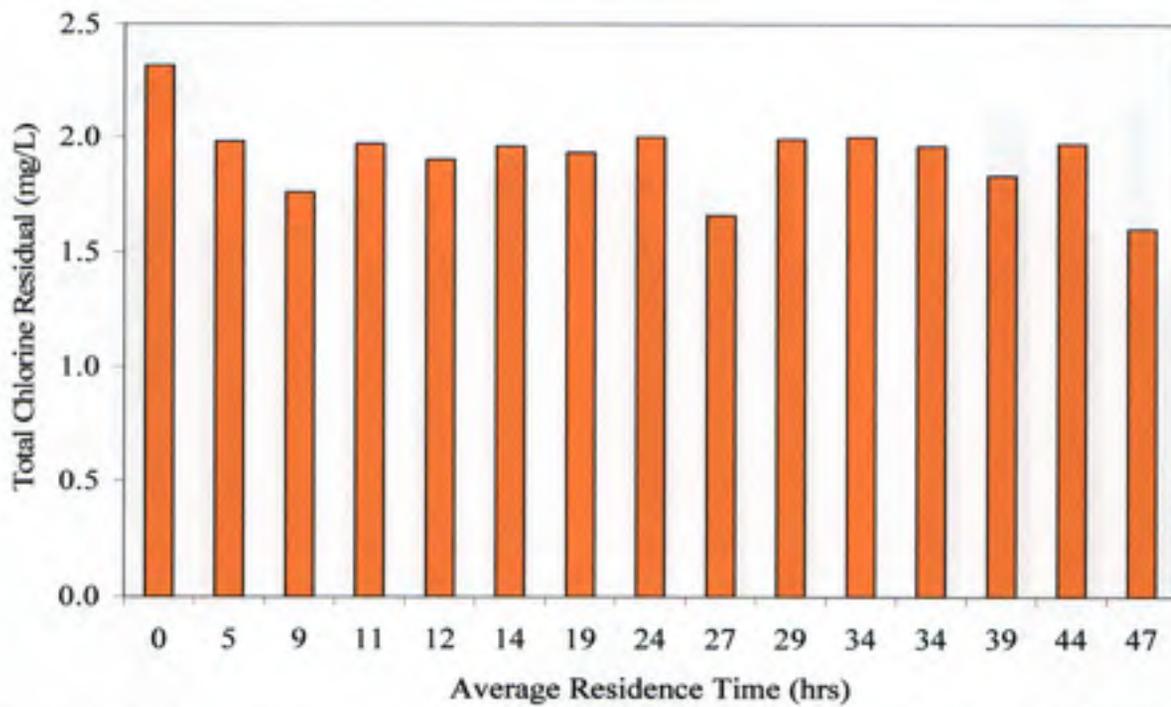


Figure C.13 Total chlorine residual versus average residence time for Utility B for 2/25/03

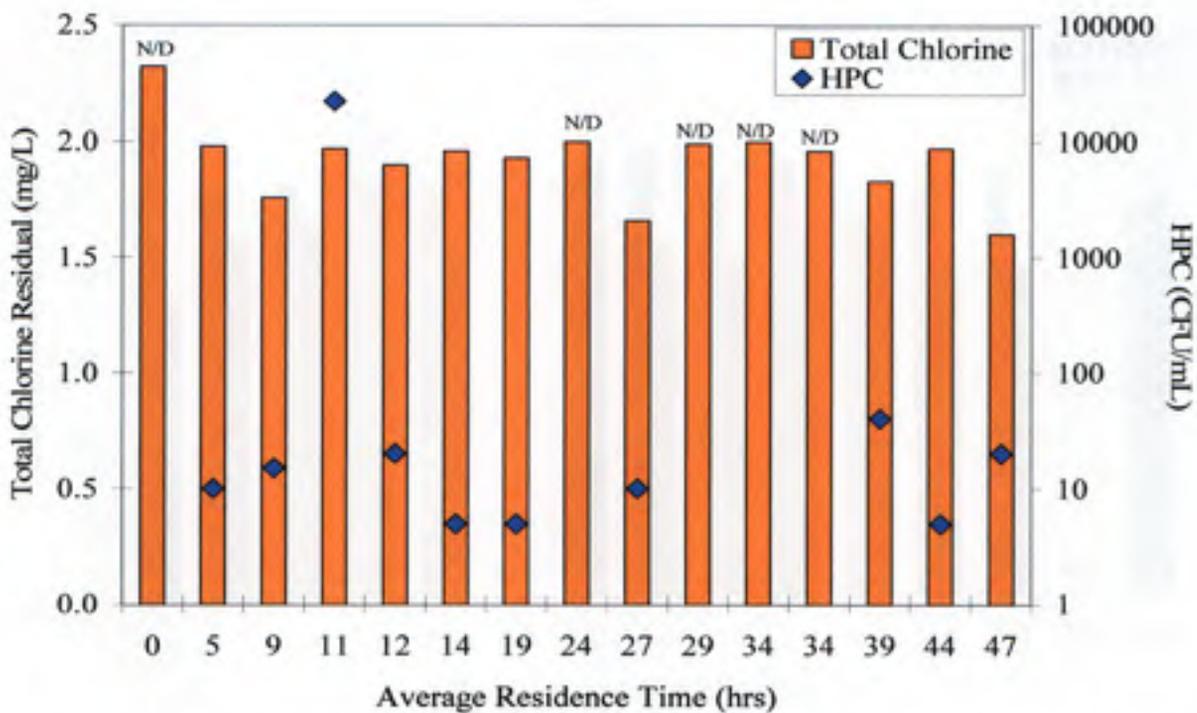


Figure C.14 Total chlorine residual and HPC versus average residence time for Utility B for 2/25/03

Table C.17

pH, temperature and chlorine data for Utility B for 6/10/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
WTP	26	8.89	1.83	2.00
308	26	8.89	2.04	2.11
883	26	8.85	1.85	1.93
975	26	8.87	1.46	1.52
979	N/S	N/S	N/S	N/S
208	26	8.92	1.41	1.56
232	26	8.90	1.63	1.66
100	26	8.94	1.76	1.88
116	26	8.98	1.50	1.6
251	26	8.92	1.66	1.76
227	26	8.96	1.10	1.15
X-3	26	8.90	1.59	1.66
R-1	26	8.92	1.68	1.76
D-6	N/S	N/S	N/S	N/S
X-11	26	8.86	1.70	1.81

Table C.18

Organic carbon and microbiological data for Utility B for 6/10/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
WTP	387	1.66	0.027	2.1E+03
308		1.78	0.031	4.2E+03
883		2.41	0.038	1.1E+03
975		1.97	0.033	6.9E+02
979		N/S	N/S	N/S
208		1.78	0.027	1.0E+03
232		1.68	0.027	1.2E+03
100		2.08	0.030	1.0E+03
116		1.91	0.026	1.8E+02
251		2.30	0.033	1.8E+02
227		2.16	0.030	1.5E+02
X-3		1.79	0.030	6.7E+02
R-1		2.11	0.030	1.4E+02
D-6		N/S	N/S	N/S
X-11		2.29	0.031	3.1E+02

Table C.19

Trihalomethane (THM) data (in µg/L) for Utility B for 6/10/03

Sample ID	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	THM4
WTP	62	12	2	<1	76
308	62	12	2	<1	76
883	68	13	2	<1	83
975	69	13	2	<1	84
979	N/S	N/S	N/S	N/S	N/S
208	77	13	2	<1	92
232	82	14	2	<1	98
100	83	14	2	<1	99
116	109	15	2	<1	126
251	83	14	2	<1	99
227	102	15	2	<1	119
X-3	74	12	2	<1	88
R-1	64	12	2	<1	78
D-6	N/S	N/S	N/S	N/S	N/S
X-11	67	12	2	<1	81

Table C.20

Haloacetic acid (HAA) data (in µg/L) for Utility B for 6/10/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
WTP	3	3	31	5	2	21	4	<1	<1	69
308	3	2	26	4	2	11	3	<1	<1	51
883	6	2	26	4	<1	12	3	<1	<1	53
975	<2	2	27	4	1	11	3	<1	<1	48
979	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
208	2	2	31	4	2	20	3	<1	<1	64
232	6	2	30	4	2	16	3	1	<1	64
100	3	1	28	4	<1	13	3	<1	<1	52
116	3	<1	34	4	1	21	3	<1	<1	66
251	3	2	28	4	1	11	3	<1	<1	52
227	3	<1	37	5	<1	24	3	<1	<1	72
X-3	6	2	37	5	2	21	3	<1	<1	76
R-1	8	2	35	5	2	23	4	1	<1	80
D-6	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
X-11	2	2	29	3	2	10	3	<1	<1	51

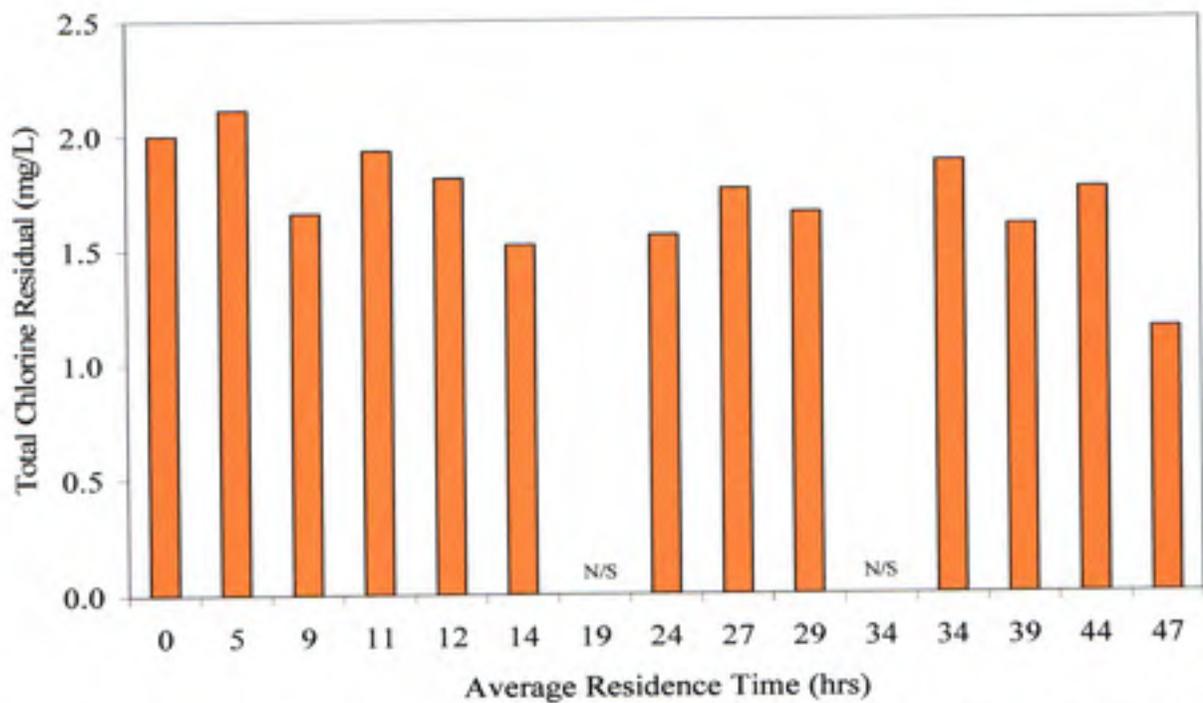


Figure C.17 Total chlorine residual versus average residence time for Utility B for 6/10/03

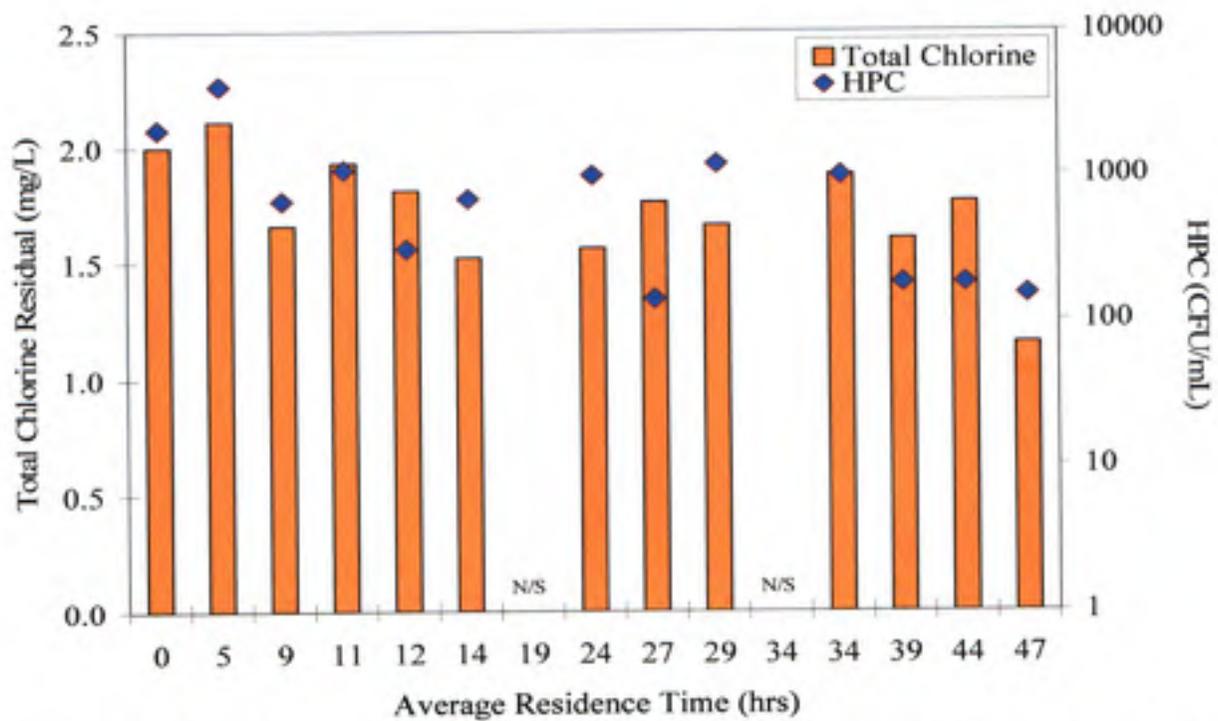


Figure C.18 Total chlorine residual and HPC versus average residence time for Utility B for 6/10/03

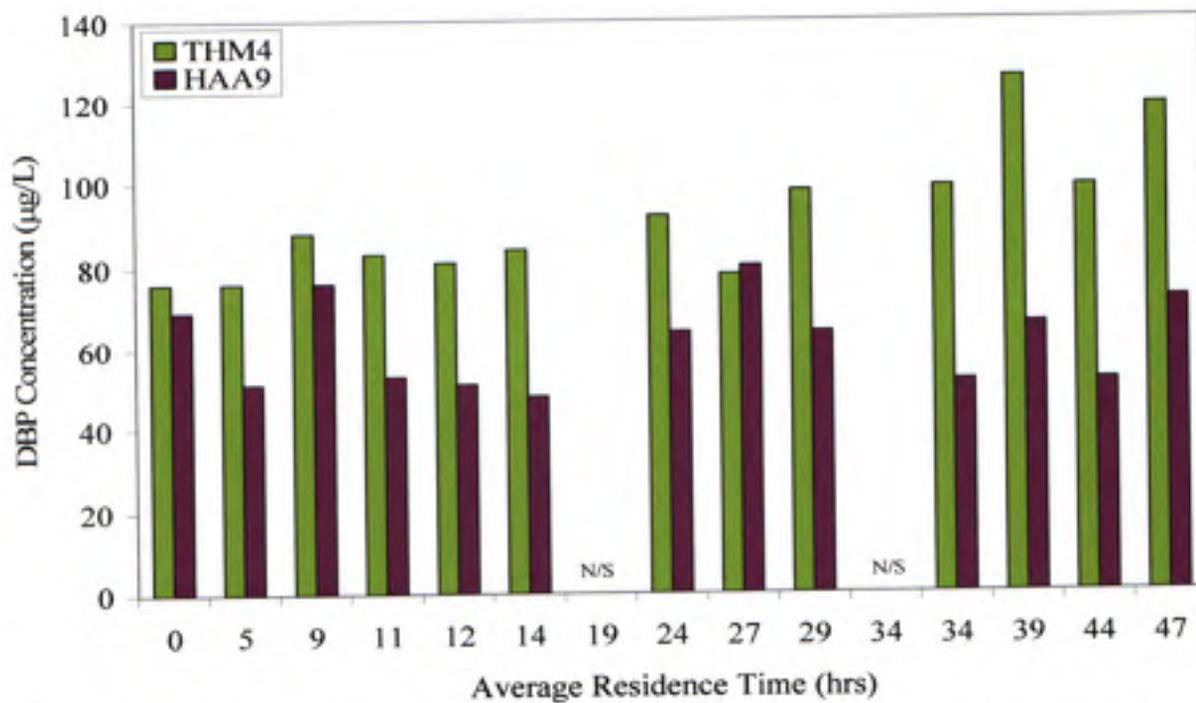


Figure C.19 THM4 and HAA9 versus average residence time for Utility B for 6/10/03

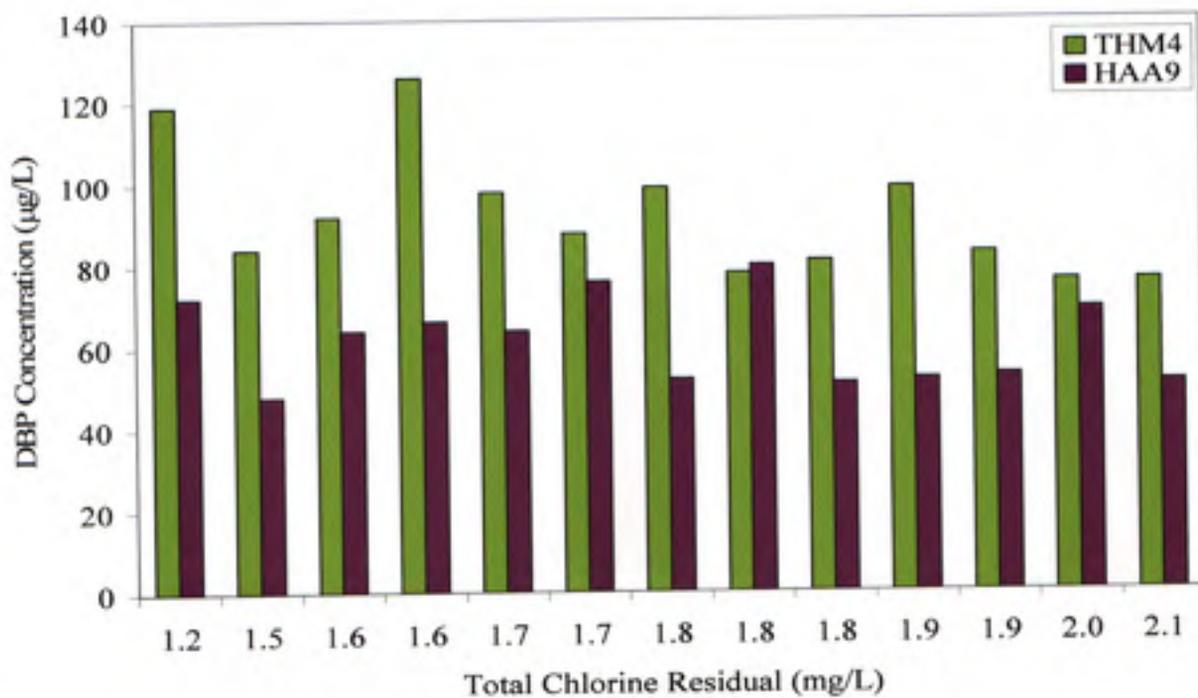


Figure C.20 THM4 and HAA9 versus total chlorine residual for Utility B for 6/10/03

Table C.21

pH, temperature and chlorine data for Utility B for 8/12/03

Sample ID	Temperature		Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
	(°C)	pH		
WTP	27	9.1	1.84	1.85
308	26	8.8	1.84	1.94
883	27	9.0	2.00	2.10
975	26	9.0	1.89	1.99
979	26	9.0	1.76	1.86
208	26	9.0	1.78	1.85
232	26	9.0	1.76	1.84
100	26	9.0	1.82	1.90
116	26	9.0	1.32	1.42
251	26	9.0	1.72	1.82
227	26	9.1	0.92	1.10
X-3	26	9.1	1.76	1.86
R-1	26	9.1	1.62	1.72
D-6	26	9.0	1.42	1.50
X-11	26	9.1	1.75	1.85

Table C.22

Organic carbon and microbiological data for Utility B for 8/12/03

Sample ID	Organic carbon and microbiological data			
	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
WTP	399	1.48	0.029	<10
308		1.53	0.028	1.0E+01
883		1.48	0.026	<10
975		1.49	0.028	6.0E+01
979		N/S	N/S	2.0E+01
208		1.49	0.023	1.0E+01
232		1.57	0.024	2.0E+01
100		1.46	0.024	2.0E+01
116		1.73	0.024	2.5E+02
251		1.58	0.024	2.0E+01
227		2.11	0.023	<10
X-3		1.45	0.027	3.0E+01
R-1		1.50	0.028	
D-6		N/S	N/S	4.0E+01
X-11		1.44	0.027	2.0E+03

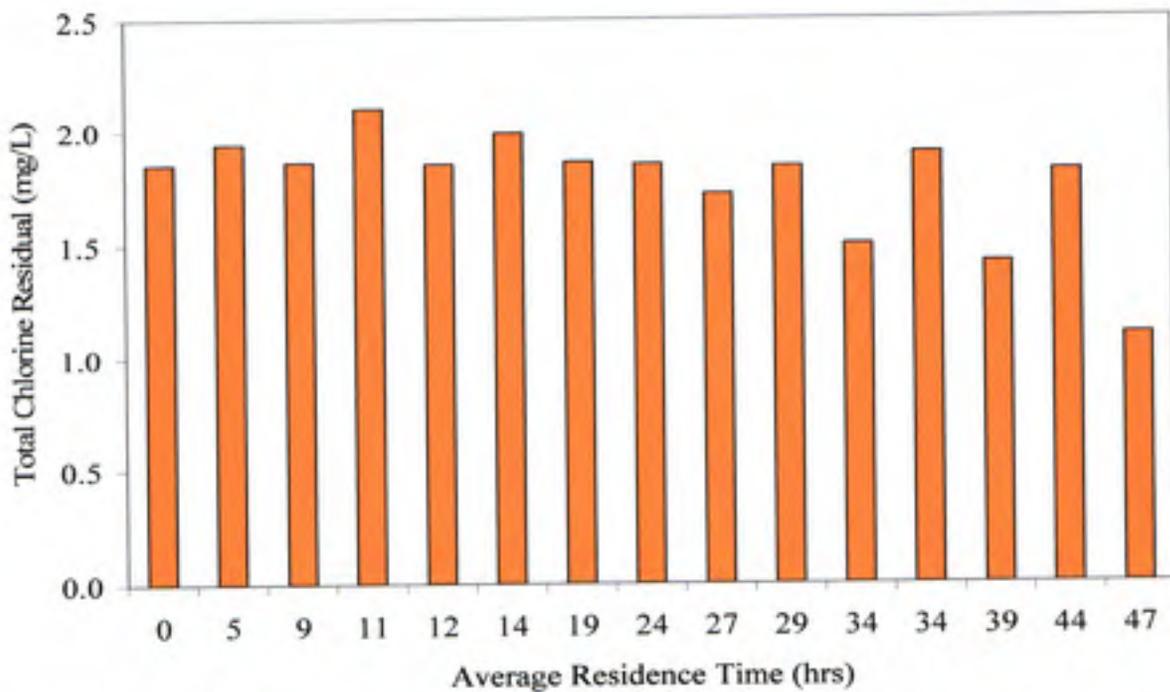


Figure C.21 Total chlorine residual versus average residence time for Utility B for 8/12/03

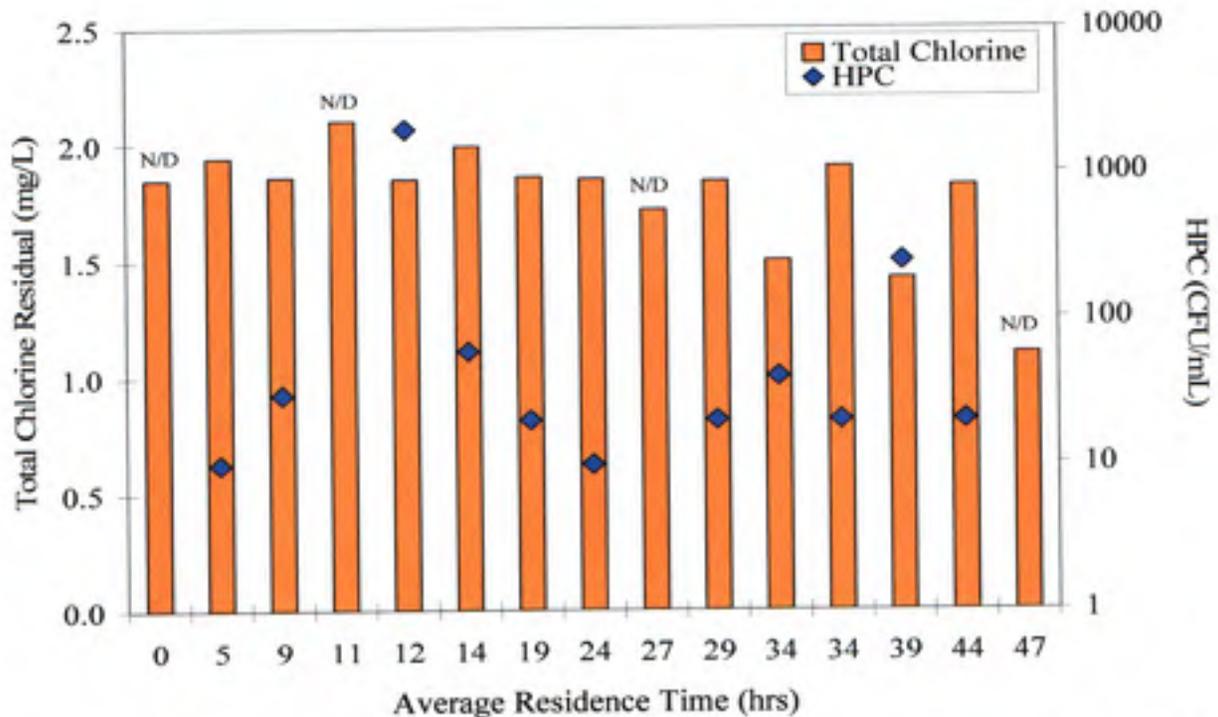


Figure C.22 Total chlorine residual and HPC versus average residence time for Utility B for 8/12/03

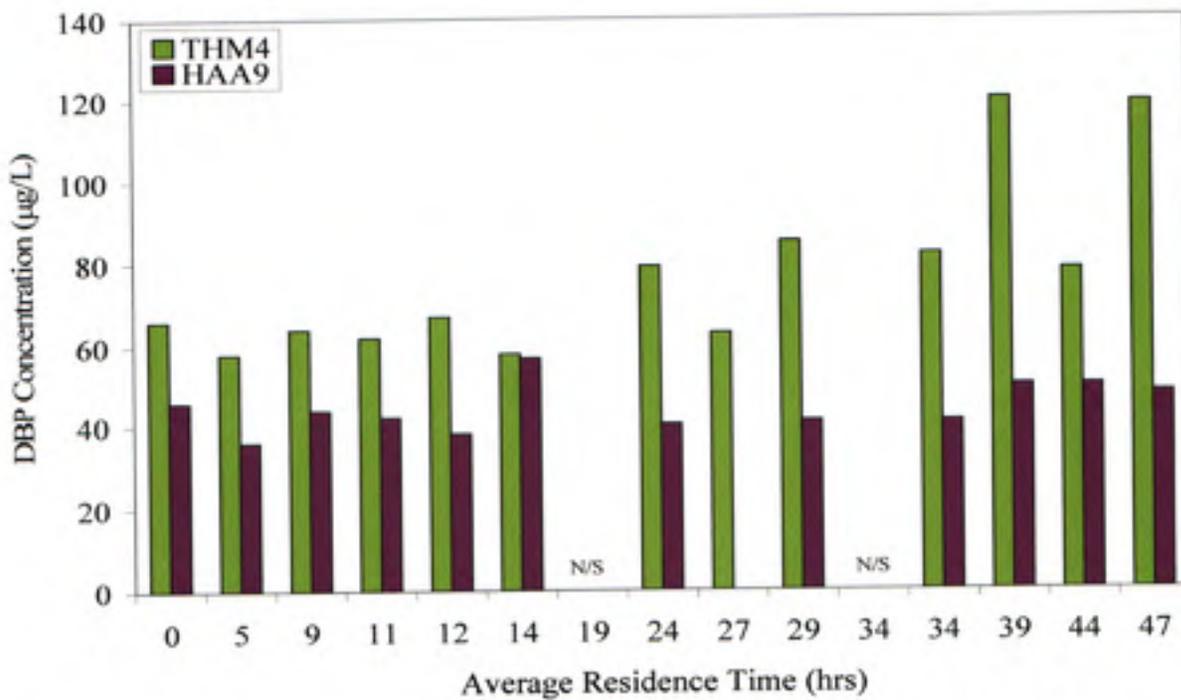


Figure C.23 THM4 and HAA9 versus average residence time for Utility B for 8/12/03

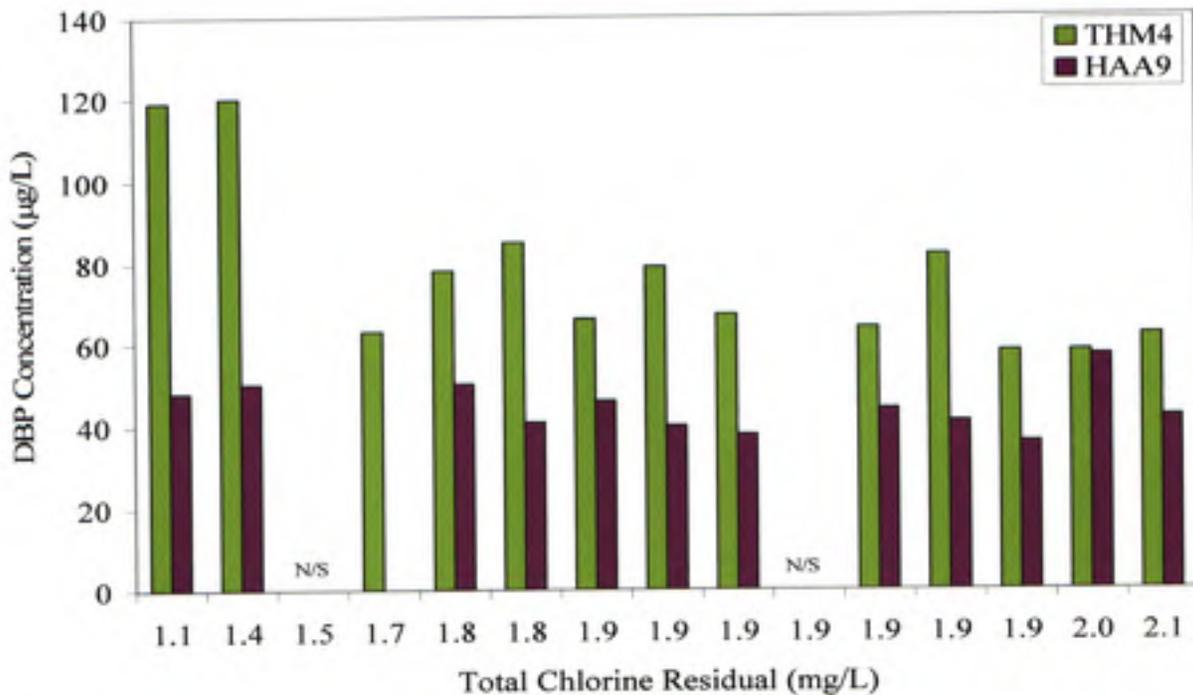


Figure C.24 THM4 and HAA9 versus total chlorine residual for Utility B for 8/12/03

Table C.25

pH, temperature and chlorine data for Utility B for 10/21/03

Sample ID	Temperature (°C)	pH	Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
WTP	22	8.80	1.98	2.10
308	20	8.80	1.78	1.85
883	20	8.86	1.51	1.60
975	20	8.83	1.65	1.73
979	20	8.93	1.65	1.73
208	21	8.82	1.73	1.83
232	20	8.82	1.81	1.92
100	21	8.85	1.61	1.68
116	21	8.86	1.73	1.80
251	21	8.80	1.54	1.60
227	22	8.81	1.70	1.80
X-3	20	9.01	1.45	1.55
R-1	20	8.87	1.61	1.70
D-6	20	8.86	1.70	1.80
X-11	20	8.88	1.72	1.83

Table C.26

Organic carbon and microbiological data for Utility B for 10/21/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)
WTP	71	1.40	0.020	NA
308		1.40	0.018	1.0E+01
883		1.41	0.019	3.0E+01
975		1.40	0.018	3.0E+01
979		N/S	N/S	7.5E+01
208		1.40	0.018	<10
232		1.40	0.021	<10
100		1.42	0.018	4.5E+01
116		1.41	0.018	<10
251		1.38	0.019	<10
227		1.37	0.019	<10
X-3		1.40	0.018	<10
R-1		1.39	0.020	
D-6		N/S	N/S	<10
X-11		1.40	0.018	<10

Table C.27

Trihalomethane (THM) data (in µg/L) for Utility B for 10/21/03

Sample ID	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	THM4
WTP	31	11	5	<1	47
308	31	12	5	<1	48
883	39	14	6	<1	59
975	41	15	5	<1	61
979	N/S	N/S	N/S	N/S	N/S
208	41	14	5	<1	60
232	43	15	6	<1	64
100	39	15	5	<1	59
116	75	18	6	<1	99
251	43	14	6	<1	63
227	45	15	6	<1	66
X-3	31	11	5	<1	47
R-1	32	12	5	<1	49
D-6	N/S	N/S	N/S	N/S	N/S
X-11	32	12	5	<1	49

Table C.28

Haloacetic acid (HAA) data (in µg/L) for Utility B for 10/21/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
WTP	<2	5	7	3	1	4	2	1	<1	23
308	<2	5	8	3	1	4	2	1	<1	24
883	<2	4	9	4	1	6	3	1	<1	28
975	<2	3	8	3	1	5	3	1	<1	24
979	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
208	<2	4	10	4	2	6	3	1	<1	30
232	<2	11	9	4	1	5	3	1	<1	34
100	<2	4	10	4	1	6	3	1	<1	29
116	<2	1	16	4	2	7	3	1	<1	34
251	<2	4	11	4	2	6	3	1	<1	31
227	<2	4	8	3	1	5	2	1	<1	24
X-3	<2	6	11	4	2	5	3	1	<1	32
R-1	<2	5	7	3	1	4	2	1		23
D-6	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
X-11	<2	5	8	3	1	5	3	1	<1	26

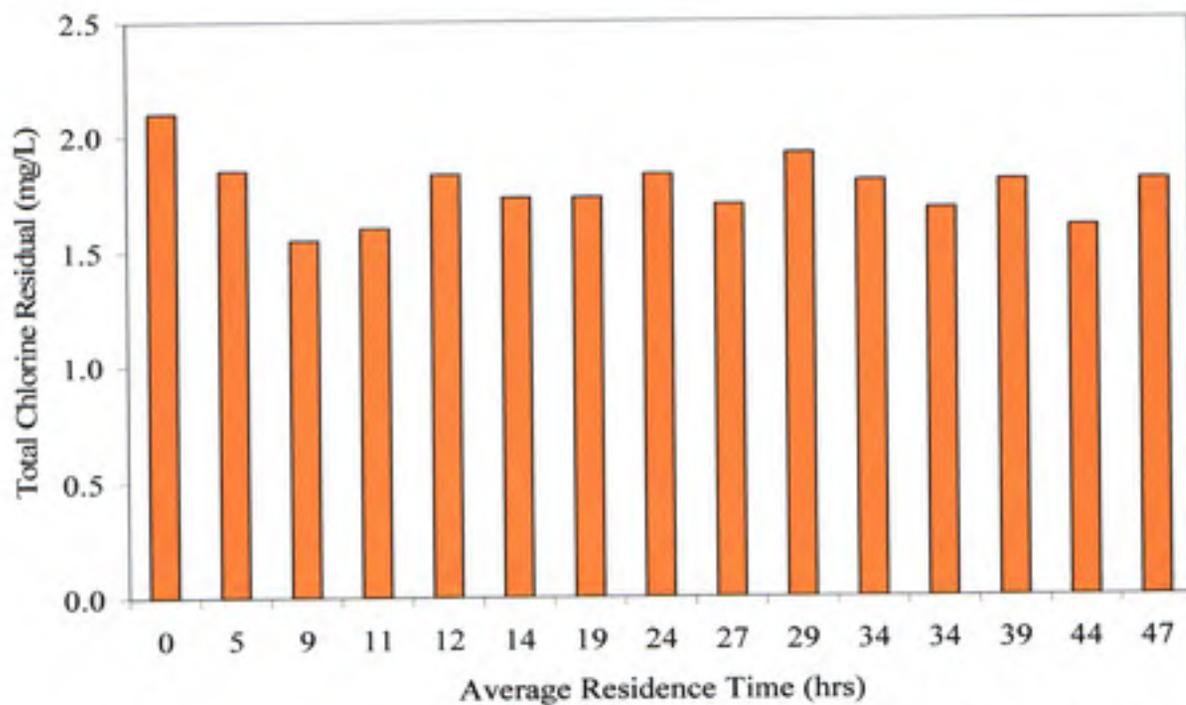


Figure C.25 Total chlorine residual versus average residence time for Utility B for 10/21/03

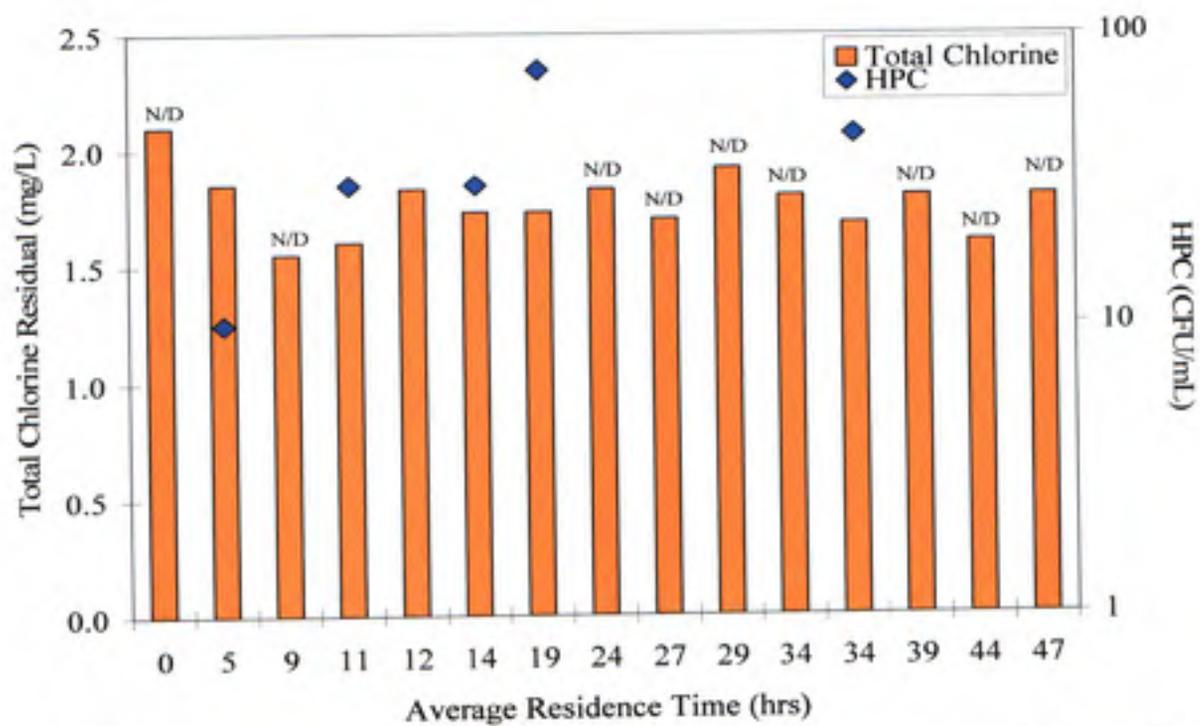


Figure C.26 Total chlorine residual and HPC versus average residence time for Utility B for 10/21/03

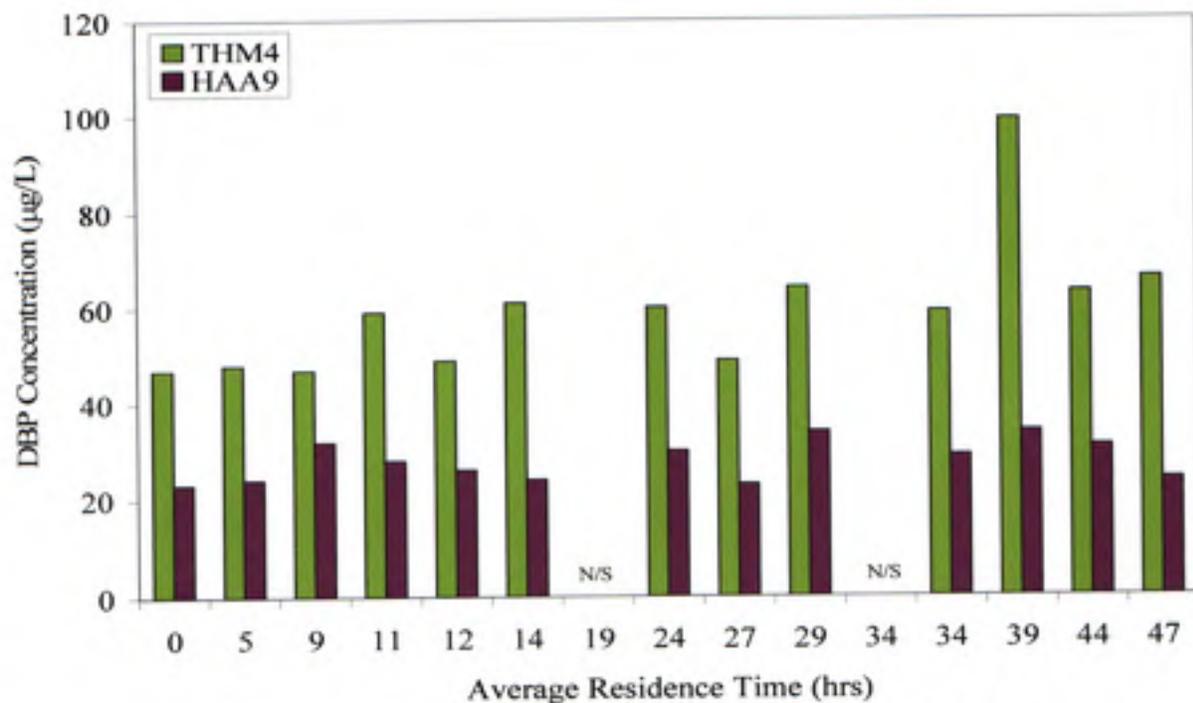


Figure C.27 THM4 and HAA9 versus average residence time for Utility B for 10/21/03

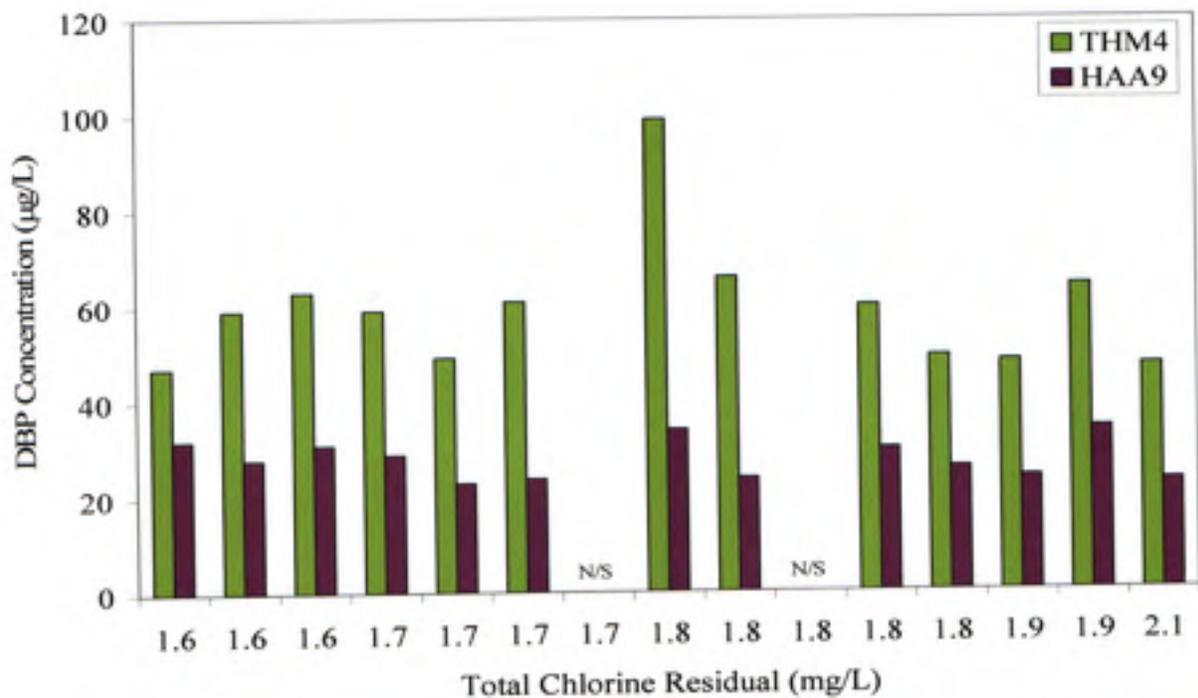


Figure C.28 THM4 and HAA9 versus total chlorine residual for Utility B for 10/21/03

**APPENDIX D**  
**Utility D**

Table D.1

pH, temperature and chlorine data for Utility D for 11/18/02

Sample ID	Temperature		Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
	(°C)	pH		
Site 1	21	8.2	0.0	2.2
Site 2	21	7.8	0.0	1.2
Site 3	22	7.8	0.0	1.8
Site 4	21	7.8	0.0	1.7
Site 5	21	7.8	0.0	1.9
Site 6	21	7.8	0.0	1.4
Site 7	20	7.9	0.0	1.6
Site 10	22	7.6	0.0	0.1
Site 11	23	7.6	0.0	0.1
Site 14	19	7.8	0.0	0.6
Site 15	23	7.7	0.0	0.4
Site 16	18	7.7	0.0	0.1

Table D.2

Organic carbon and microbiological data for Utility D for 11/18/02

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)	Bromide (mg/L)
Site 1	138	1.57	0.05	<10	0.47	0.011	2.4	0.13
Site 2		0.86	0.04	4.90E+02	0.35	0.099	ND	
Site 3		1.01	0.05	4.45E+02	0.39	0.061	2.2	
Site 4		1.01	0.04	3.00E+02	0.36	0.053	2.4	
Site 5		0.96	0.05	2.90E+02	0.39	0.053	2	
Site 6		0.92 *	0.04	2.45E+02	0.31	0.040	2	
Site 7		1.18	0.05	1.90E+02	0.37	0.033	2.7	0.14
Site 10		0.55	0.04	5.20E+03	0.22	0.065	ND	0.14
Site 11		0.62	0.04	2.03E+04	0.23	0.101	ND	0.14
Site 14		0.83	0.05	1.30E+02	0.41	0.025	2.9	
Site 15		0.91	0.04	1.93E+03	0.11	0.261	3.6	0.15
Site 16		0.44	0.03	7.80E+03	0.04	0.332	3.2	

\* No replicate for this sample.

Table D.3

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility D for 11/18/02

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
Site 1	12	22	32	28	94
Site 2	8	10	14	14	46
Site 3	12	16	21	21	69
Site 4	10	14	20	19	62
Site 5	11	14	20	21	67
Site 6	10	13	18	17	58
Site 7	10	16	23	21	71
Site 10	9	8	10	9	36
Site 11	10	9	11	9	39
Site 14	10	16	23	21	69
Site 15	10	12	16	14	52
Site 16	8	6	7	6	26

Table D.4

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility D for 11/18/02

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
Site 1	<2	<2	5	9	11	3	6	6	2	43
Site 2	<2	<2	2	4	6	2	4	3	<2	23
Site 3	<2	<2	4	6	8	3	5	5	<2	32
Site 4	<2	<2	3	6	8	3	5	5	<2	29
Site 5	<2	<2	4	6	9	4	5	5	<2	33
Site 6	<2	<2	3	5	7	3	5	5	<2	27
Site 7	<2	<2	4	7	9	3	6	6	<2	35
Site 10	<2	<2	<2	<2	<2	3	4	3	<2	9
Site 11	<2	<2	<2	<2	<2	3	4	3	<2	9
Site 14	<2	<2	4	8	10	3	7	7	3	41
Site 15	<2	<2	<2	3	4	3	4	4	3	20
Site 16	<2	<2	<2	<2	<2	2	3	3	3	11

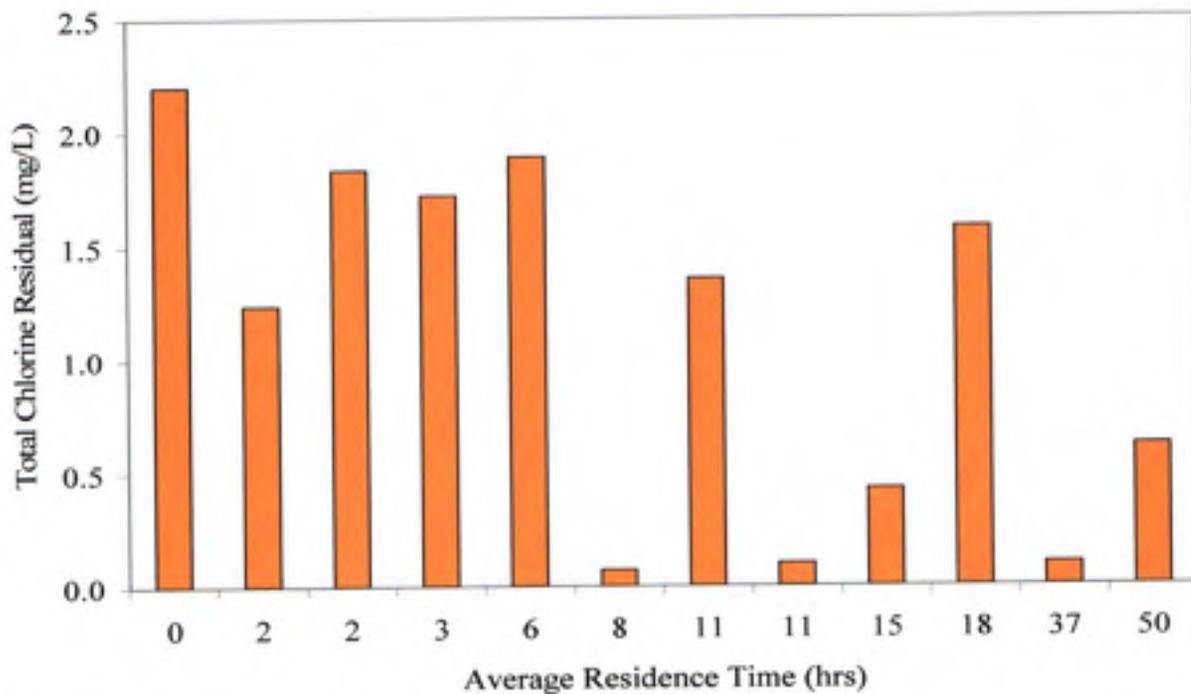


Figure D.1 Total chlorine residual versus average residence time for Utility D for 11/18/02

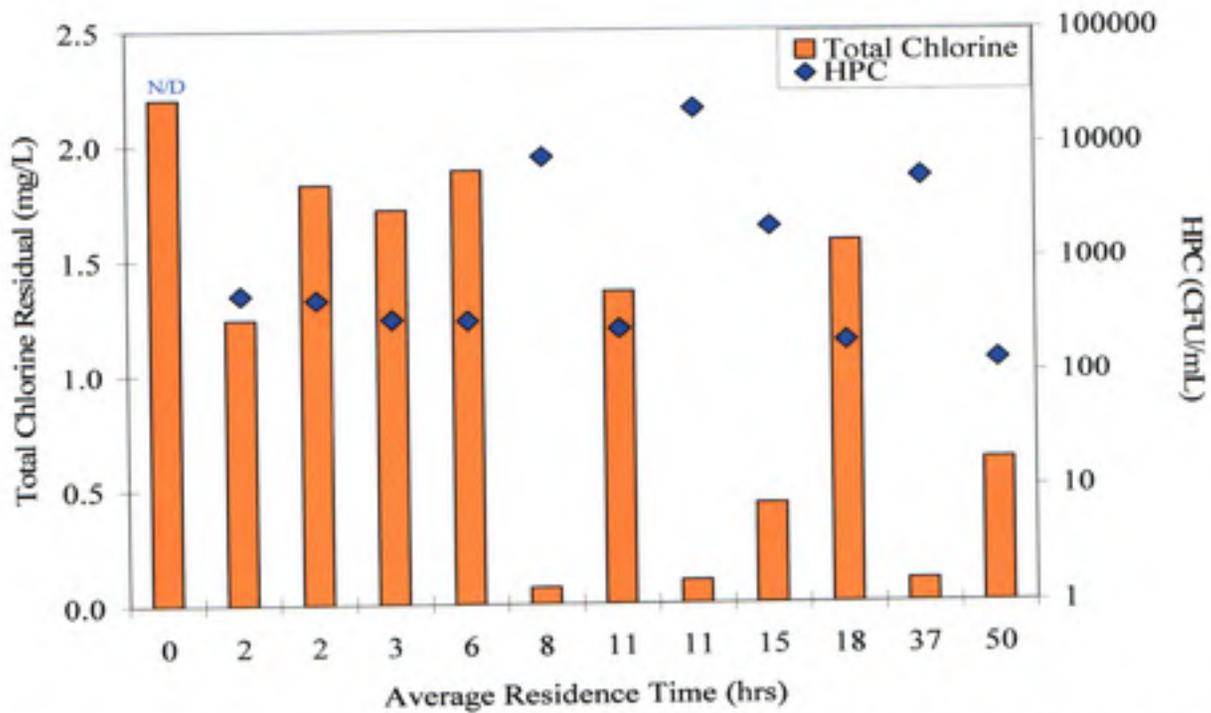


Figure D.2 Total chlorine residual and HPC versus average residence time for Utility D for 11/18/02

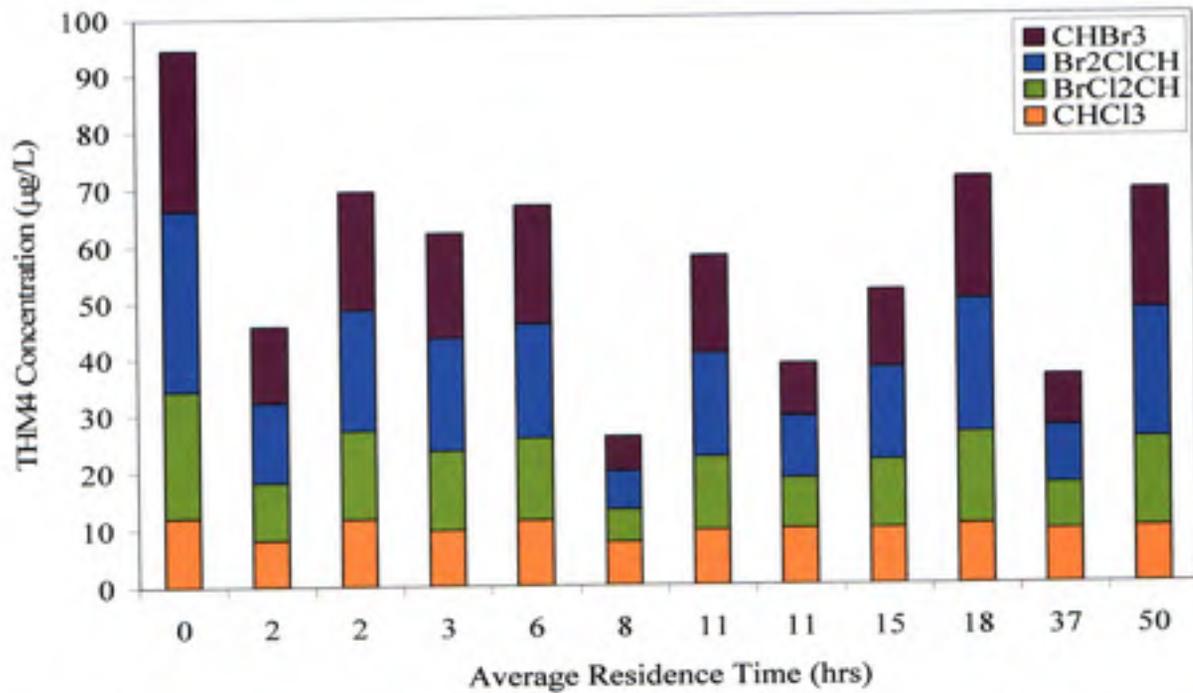


Figure D.3 THM4 speciation versus average residence time for Utility D for 11/18/02

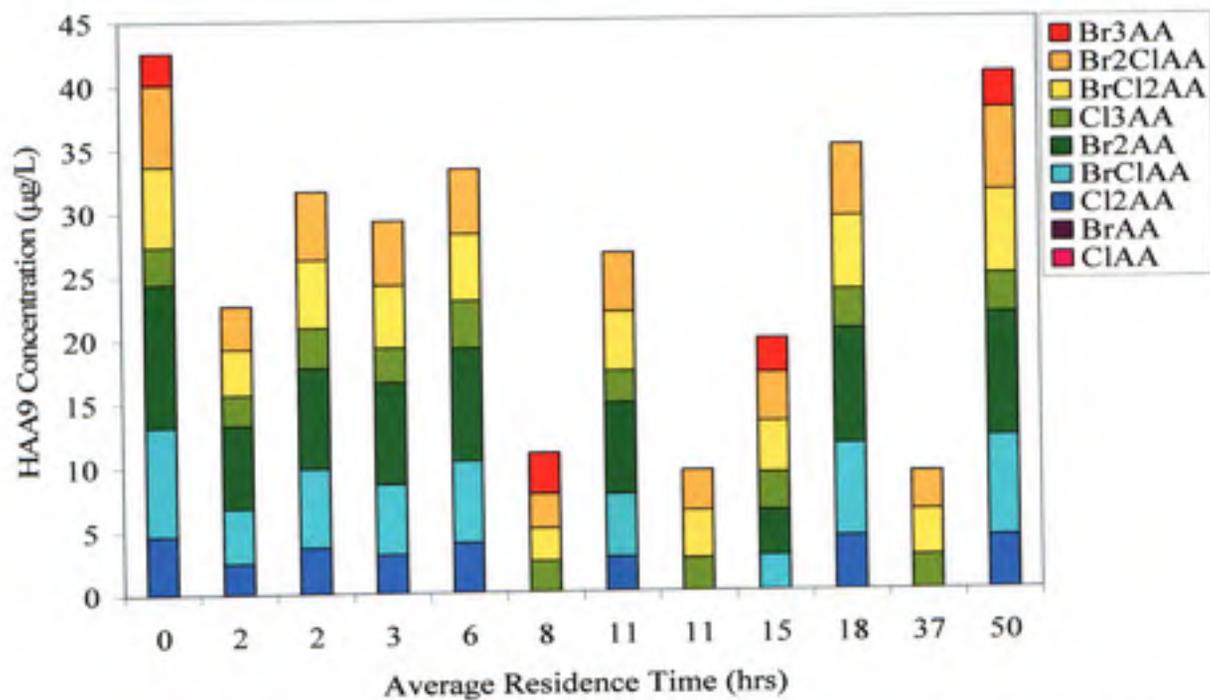


Figure D.4 HAA9 speciation versus average residence time for Utility D for 11/18/02

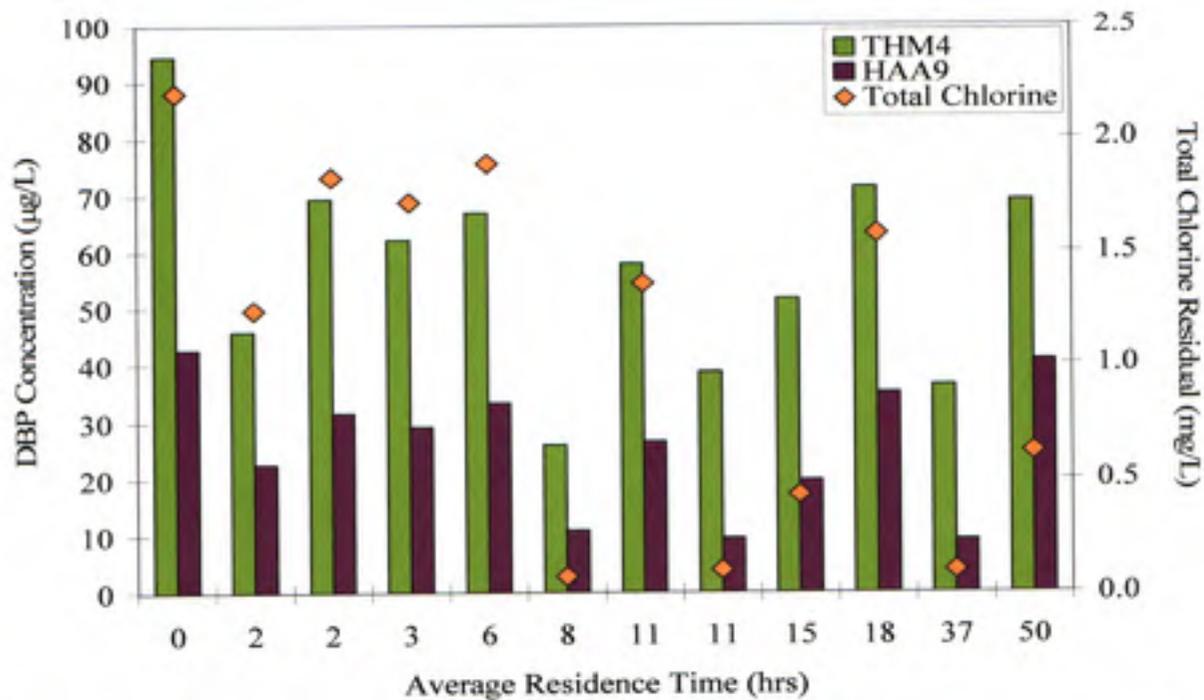


Figure D.5 THM4, HAA9 and total chlorine residual versus average residence time for Utility D for 11/18/02

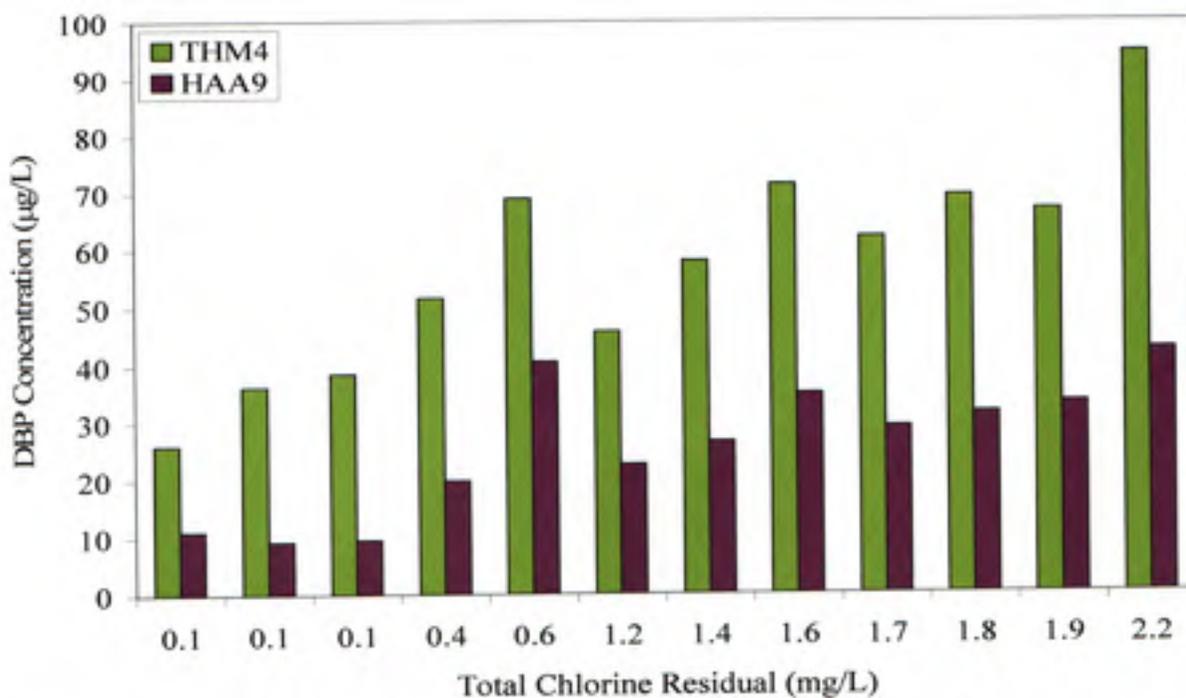


Figure D.6 THM4 and HAA9 concentrations versus total chlorine residual for Utility D for 11/18/02

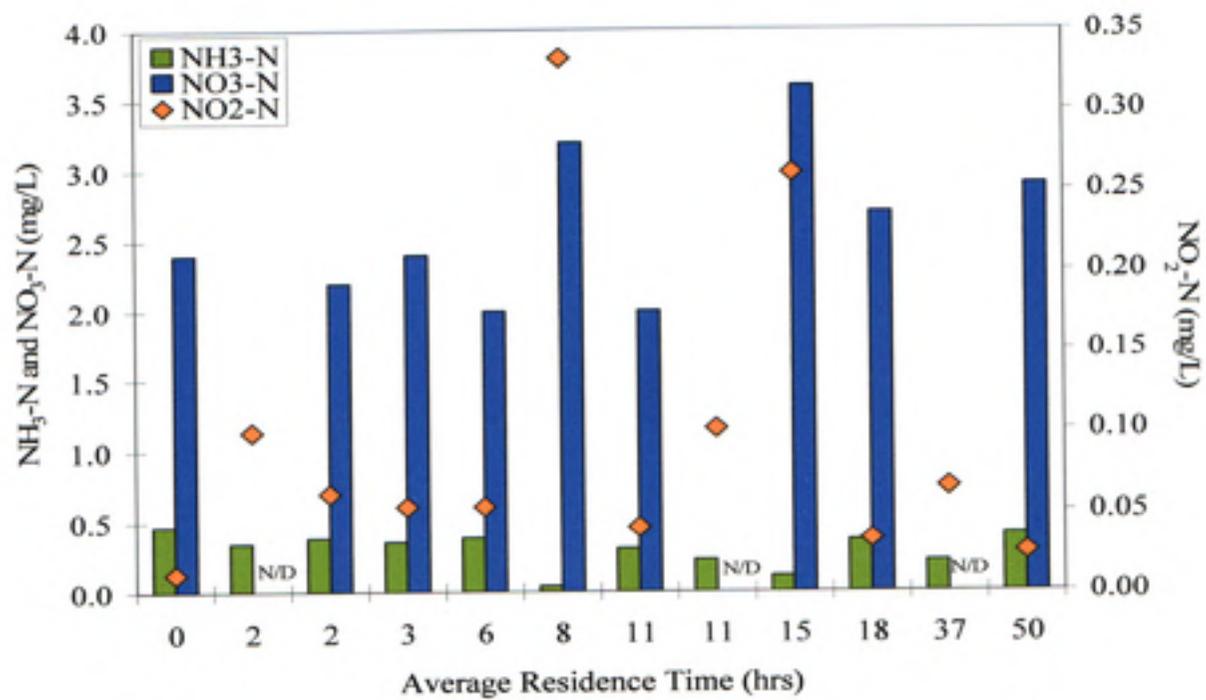


Figure D.7 Nitrogen species versus total chlorine residual for Utility D for 11/18/02

Table D.5

pH, temperature and chlorine data for Utility D for 6/10/03

Sample ID	Temperature		Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
	(°C)	pH		
Site 2	22	7.8	0.0	1.1
Site 3	23	7.8	0.0	1.1
Site 4	21	7.8	0.0	1.0
Site 5	21	7.8	0.0	1.1
Site 6	21	7.9	0.0	1.5
Site 7	22	8.0	0.0	1.9
Site 8	21	7.8	0.0	1.3
Site 9	20	7.7	0.0	0.5
Site 10	21	8.0	1.9	2.6
Site 12	18	8.1	2.8	2.8
Site 13	21	7.2	0.0	0.1

Table D.6

Organic carbon and microbiological data for Utility D for 6/10/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)	Bromide (mg/L)
Site 2				6.20E+02	0.15	0.002	0.0	
Site 3				2.20E+03	0.18	0.006	0.0	0.16
Site 4				3.00E+03	0.18	0.004	0.0	
Site 5				3.30E+03	0.20	0.00	0.0	
Site 6				3.25E+02	0.18	0.022	0.0	
Site 7				2.00E+03	0.40	0.023	3.2	0.17
Site 8				2.60E+03	0.25	0.121	2.3	0.20
Site 9				1.90E+03	0.17	0.244	2.4	
Site 10				3.70E+03	0.50	0.003	3.3	0.15
Site 12	107	1.71	0.05	2.70E+03	0.50	0.010	3.1	0.15
Site 13				2.90E+03	0.11	0.072	3.3	0.20

Table D.7

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility D for 6/10/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
Site 2	18	32	48	23	120
Site 3	16	30	45	23	114
Site 4	16	31	46	23	115
Site 5	15	29	44	22	110
Site 6	16	32	47	23	117
Site 7	5	20	30	12	68
Site 8	2	11	16	7	37
Site 9	2	10	15	6	34
Site 10	5	21	31	12	69
Site 12	6	22	33	14	74
Site 13	4	16	23	10	53

Table D.8

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility D for 6/10/03

Sample ID	CIAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
Site 2	<2	<2	6	8	10	7	9	9	4	53
Site 3	<2	<2	6	8	10	6	8	8	4	49
Site 4	<2	<2	5	8	10	6	9	8	4	51
Site 5	<2	<2	5	7	10	6	9	8	4	48
Site 6	<2	<2	5	8	9	6	8	7	4	47
Site 7	4	<2	4	6	7	3	6	6	3	41
Site 8	<2	<2	2	3	4	<2	4	4	2	20
Site 9	<2	<2	<2	2	3	<2	4	3	2	14
Site 10	<2	<2	4	7	9	3	7	7	4	41
Site 12	3	<2	6	7	9	4	7	7	4	46
Site 13	<2	<2	<2	2	3	3	4	5	2	20

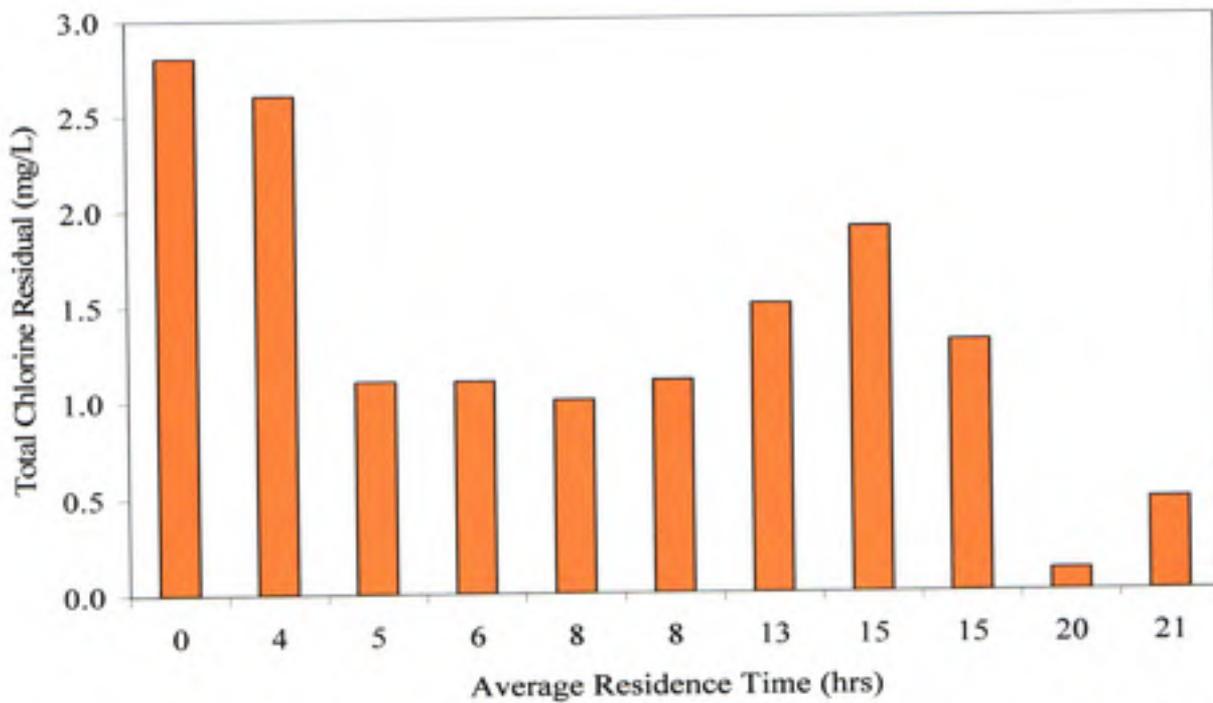


Figure D.8 Total chlorine residual versus average residence time for Utility D for 6/10/03

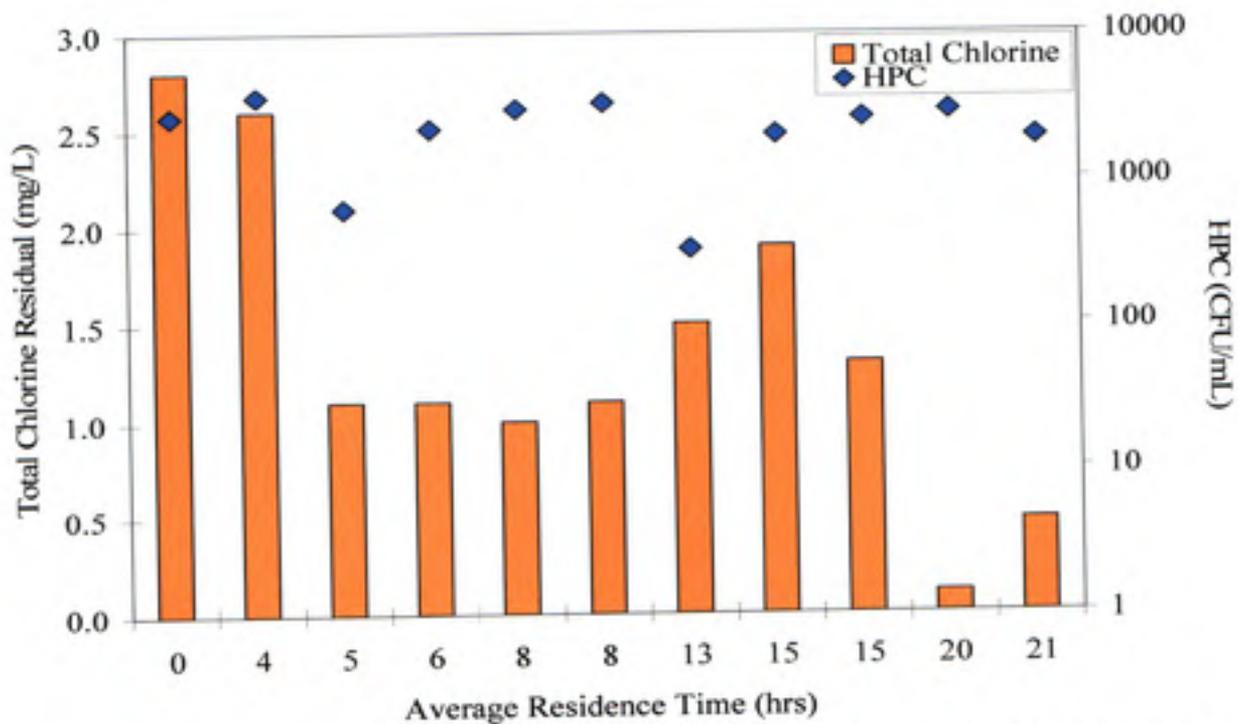


Figure D.9 Total chlorine residual and HPC versus average residence time for Utility D for 6/10/03

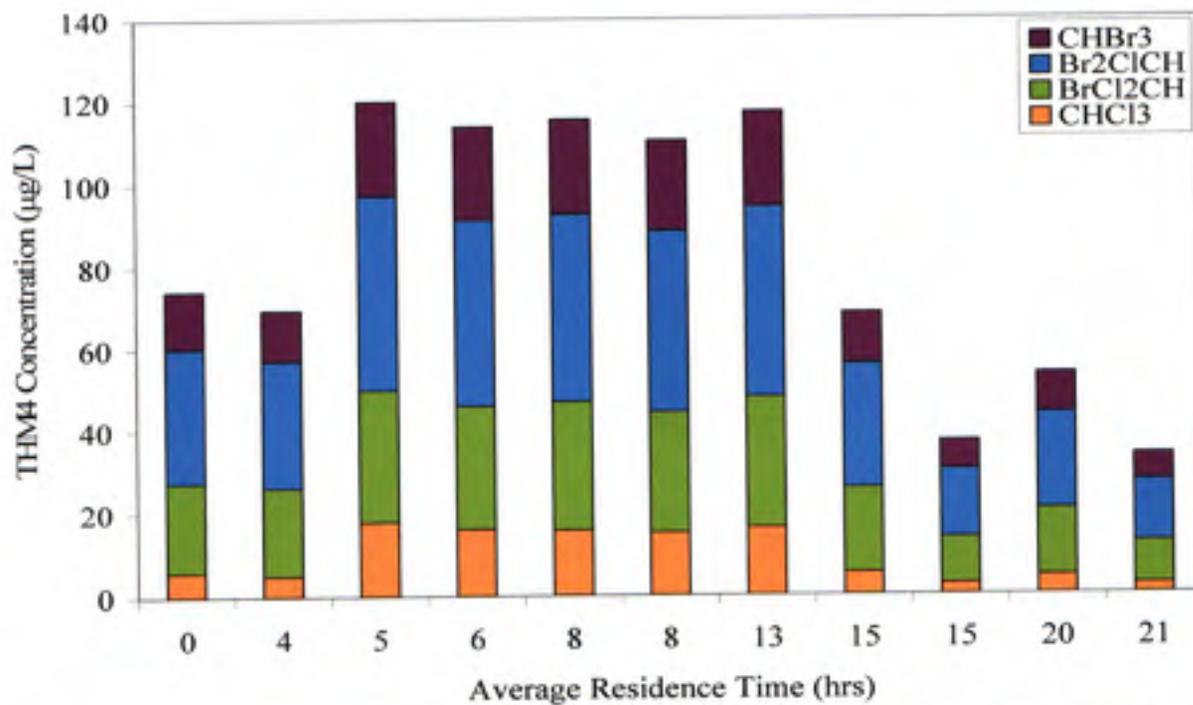


Figure D.10 THM4 speciation versus average residence time for Utility D for 6/10/03

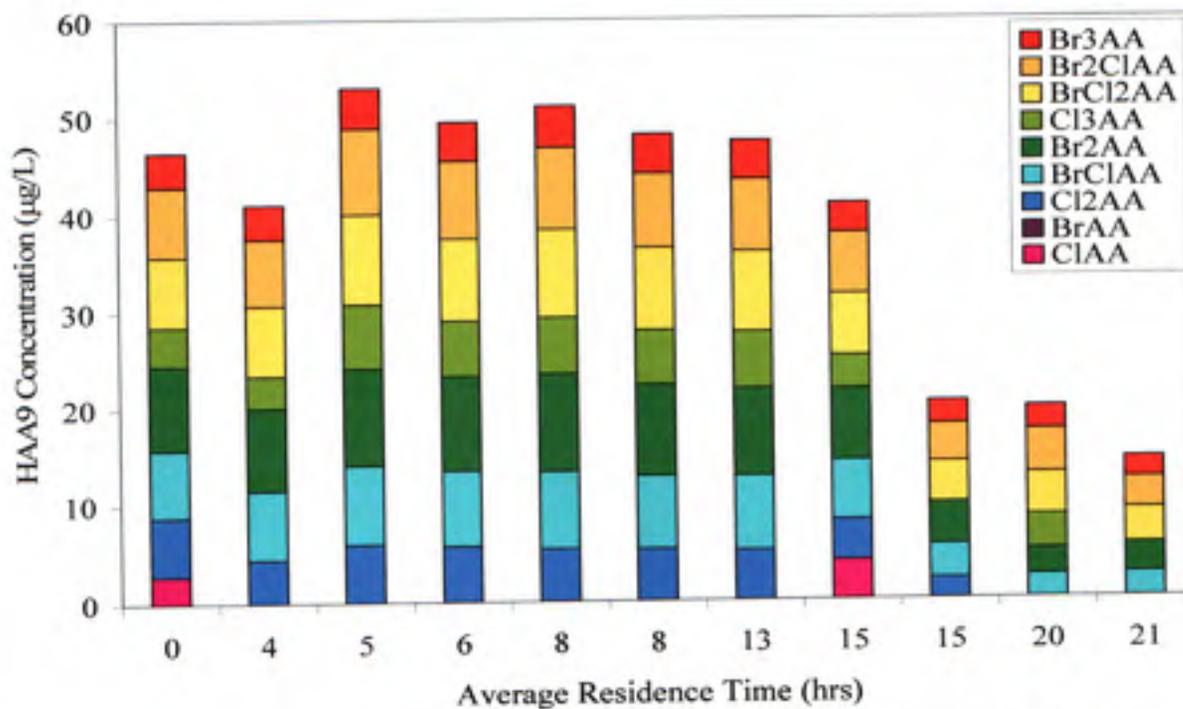


Figure D.11 HAA9 speciation versus average residence time for Utility D for 6/10/03

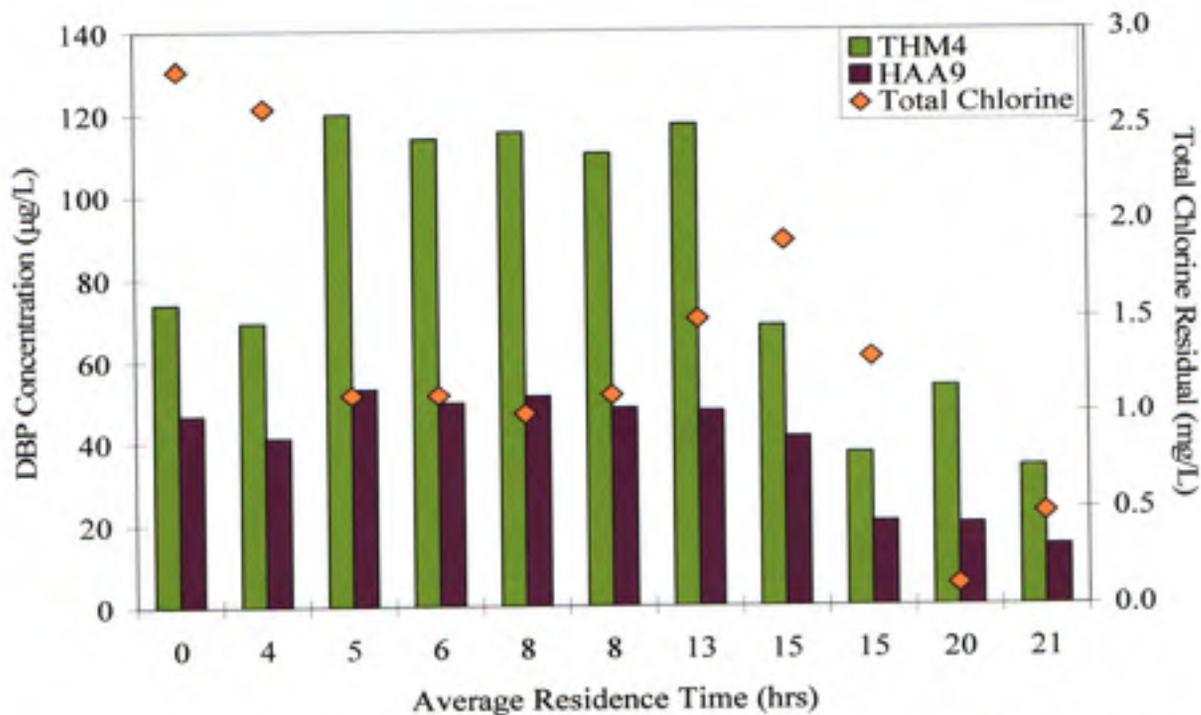


Figure D.12 THM4, HAA9 and total chlorine residual versus average residence time for Utility D for 6/10/03

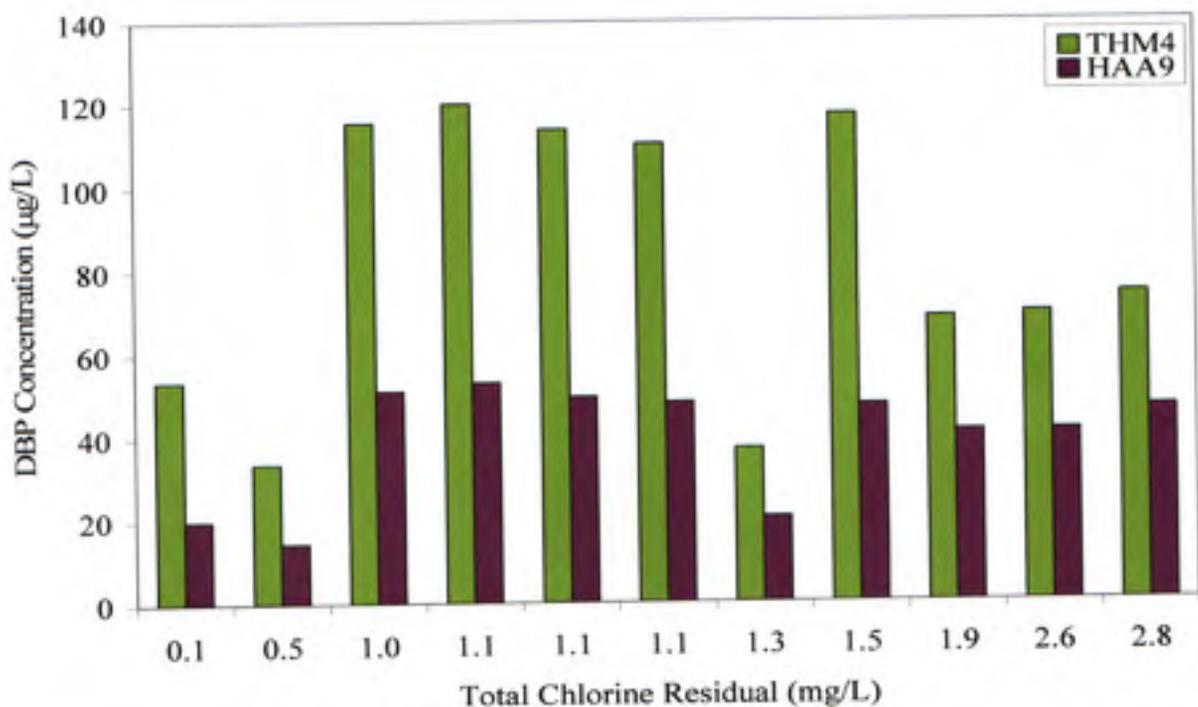


Figure D.13 THM4 and HAA9 concentration versus total chlorine residual for Utility D for 6/10/03

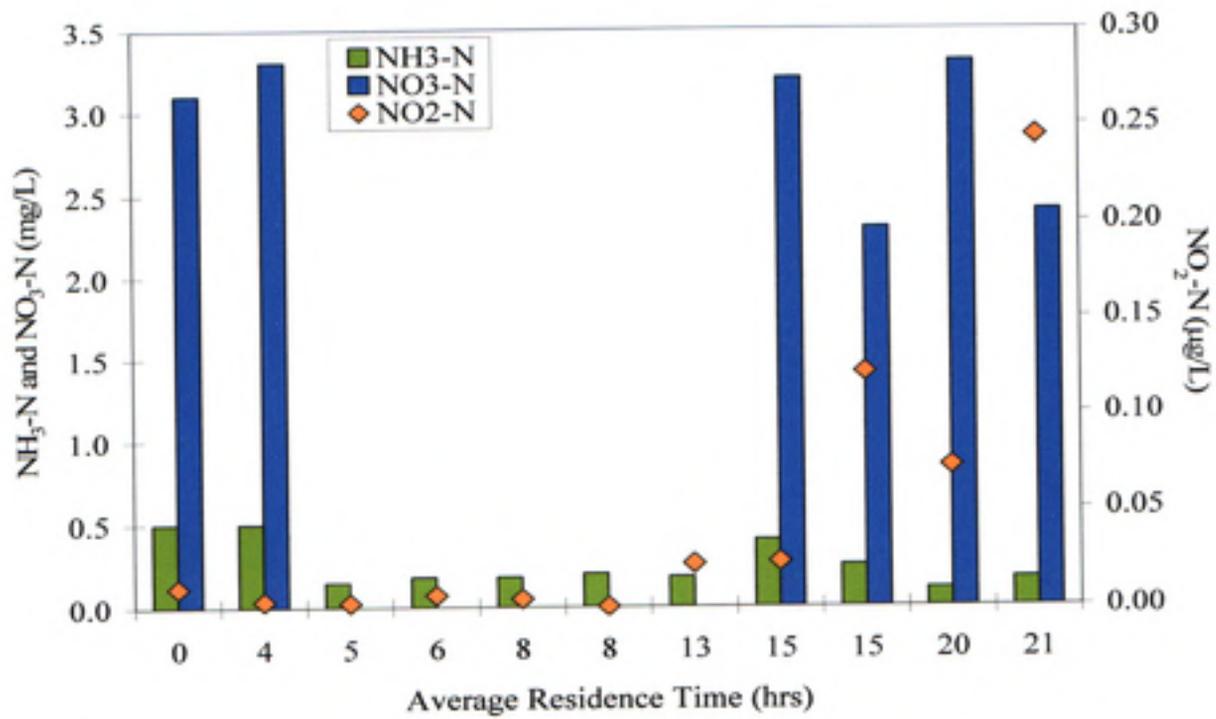


Figure D.14 Nitrogen species versus total chlorine residual for Utility D for 6/10/03

Table D.9

pH, temperature and chlorine data for Utility D for 7/22/03

Sample ID	Temperature		Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
	(°C)	pH		
Site 1	21	8.0	0.0	2.5
Site 2	22	8.0	0.0	2.5
Site 3	20	8.0	0.0	2.6
Site 4	20	8.0	0.0	2.9
Site 5	22	7.9	0.0	2.4
Site 6	23	8.0	0.0	1.3
Site 7	26	8.0	0.0	2.1
Site 8	24	7.9	0.0	1.9
Site 9	24	8.0	0.0	2.0
Site 10	26	8.0	0.0	1.2
Site 12	23	7.8	0.0	0.2
Site 13	28	8.0	0.0	0.6

Table D.10

Organic carbon and microbiological data for Utility D for 7/22/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)	Bromide (mg/L)
Site 1	126	2.58	0.05	2.5E+01	0.48	0.007	3.2	0.18
Site 2				1.5E+01	0.45	0.005	3.5	
Site 3				<10	0.43	0.006	3.2	0.18
Site 4				1.5E+01	0.46	0.009	3.1	
Site 5				6.5E+01	0.46	0.005	3.2	
Site 6				2.5E+01	0.47	0.005	2.9	
Site 7				1.5E+01	0.46	0.005	3.3	0.18
Site 8				5.0E+00	0.43	0.008	3.5	0.18
Site 9				2.5E+01	0.38	0.009	3.6	
Site 10				5.0E+00	0.43	0.007	3.3	0.18
Site 12	89	2.55	0.05	2.0E+01	0.44	0.004	3.1	0.18
Site 13				8.0E+01	0.31	0.020	3.5	0.18

Table D.11

Trihalomethane (THM) data (in  $\mu\text{g/L}$ ) for Utility D for 7/22/03

Sample ID	$\text{CHCl}_3$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	THM4
Site 1	10	21	33	9	74
Site 2	10	21	32	9	72
Site 3	10	21	32	9	72
Site 4	10	21	33	9	73
Site 5	10	21	33	9	74
Site 6	10	21	33	9	74
Site 7	10	21	33	9	74
Site 8	10	21	33	9	73
Site 9	10	21	33	9	74
Site 10	10	21	33	9	74
Site 12	10	21	33	9	73
Site 13	11	21	33	9	75

Table D.12

Haloacetic acid (HAA) data (in  $\mu\text{g/L}$ ) for Utility D for 7/22/03

Sample ID	CIAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
Site 1	<2	<2	5	7	8	3	6	7	4	41
Site 2	<2	<2	5	7	8	3	6	7	3	40
Site 3	<2	<2	5	7	9	3	6	7	4	41
Site 4	<2	<2	5	7	8	3	6	7	3	40
Site 5	<2	<2	5	7	8	3	6	7	4	41
Site 6	<2	<2	5	7	8	3	6	7	3	41
Site 7	<2	<2	5	7	8	3	7	6	3	40
Site 8	<2	<2	5	7	8	3	8	6	5	42
Site 9	<2	<2	5	7	8	3	6	7	3	39
Site 10	<2	<2	5	8	9	3	6	8	3	42
Site 12	<2	<2	<2	8	9	<2	7	8	4	35
Site 13	<2	<2	5	8	8	3	7	7	3	41

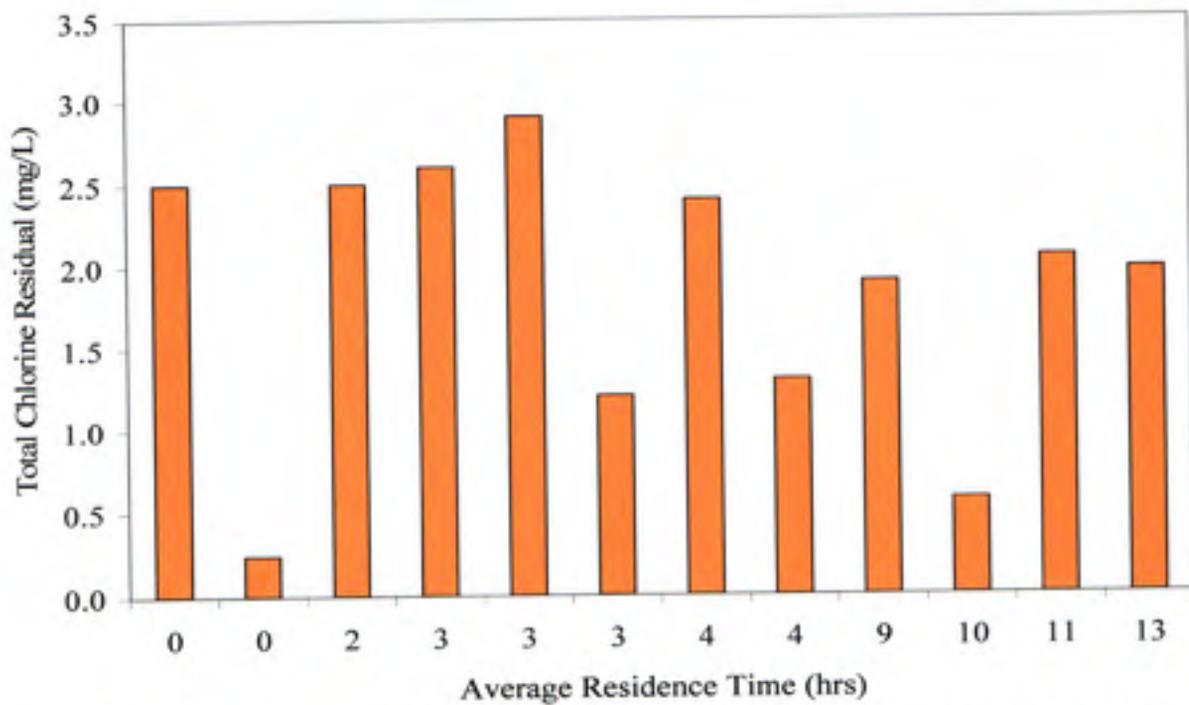


Figure D.15 Total chlorine residual versus average residence time for Utility D for 7/22/03

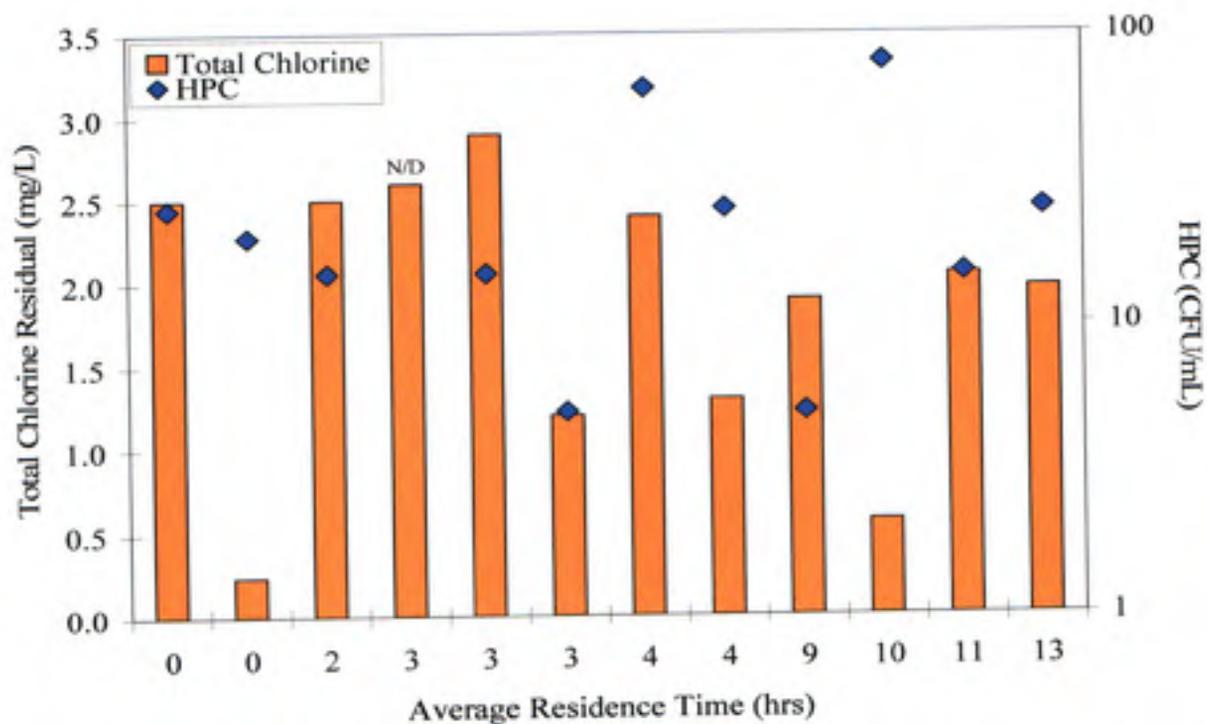


Figure D.16 Total chlorine residual and HPC versus average residence time for Utility D for 7/22/03

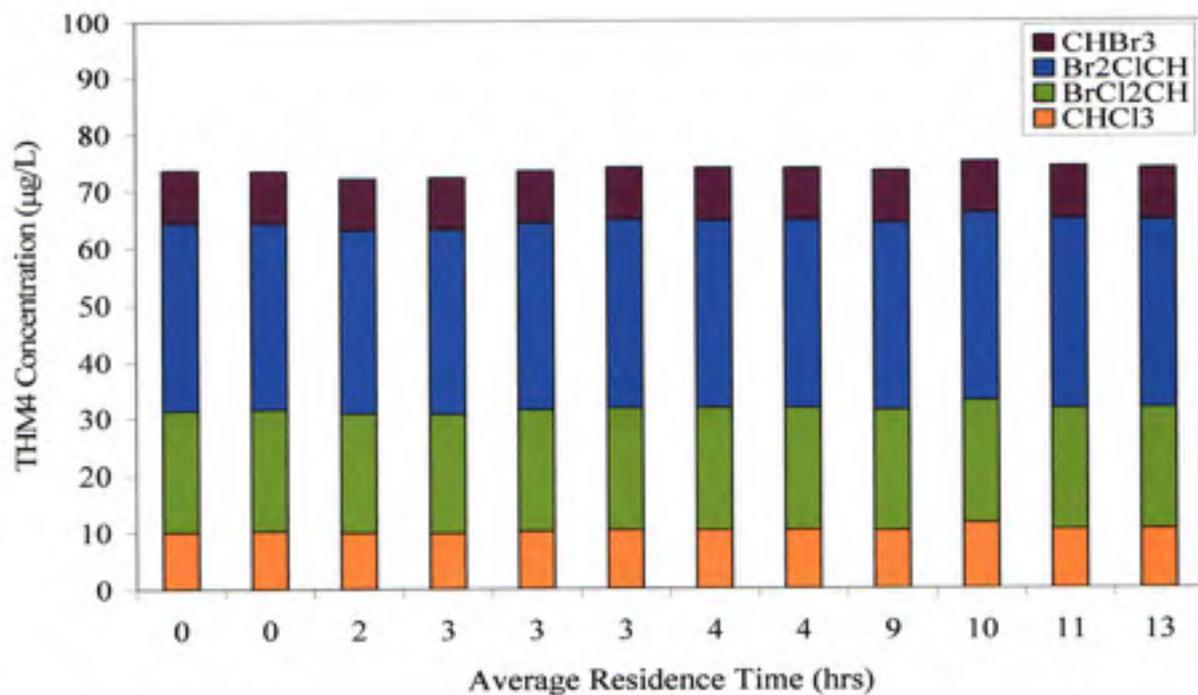


Figure D.17 THM4 speciation versus average residence time for Utility D for 7/22/03

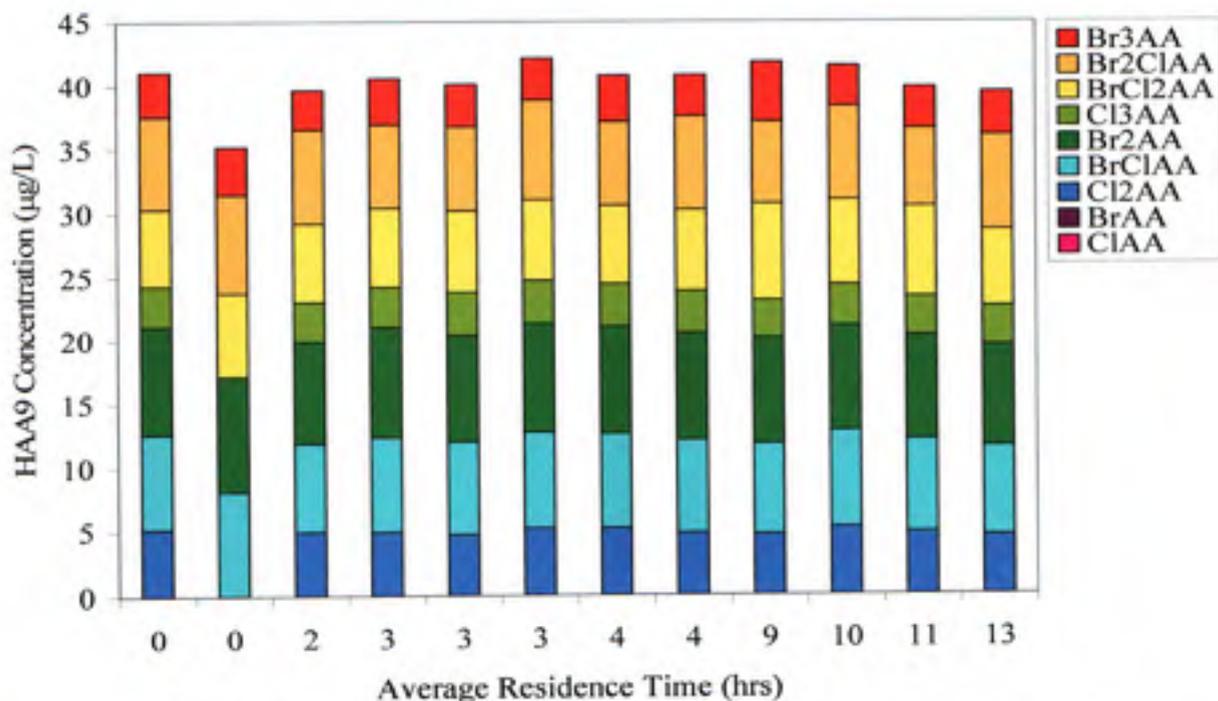


Figure D.18 HAA9 speciation versus average residence time for Utility D for 7/22/03

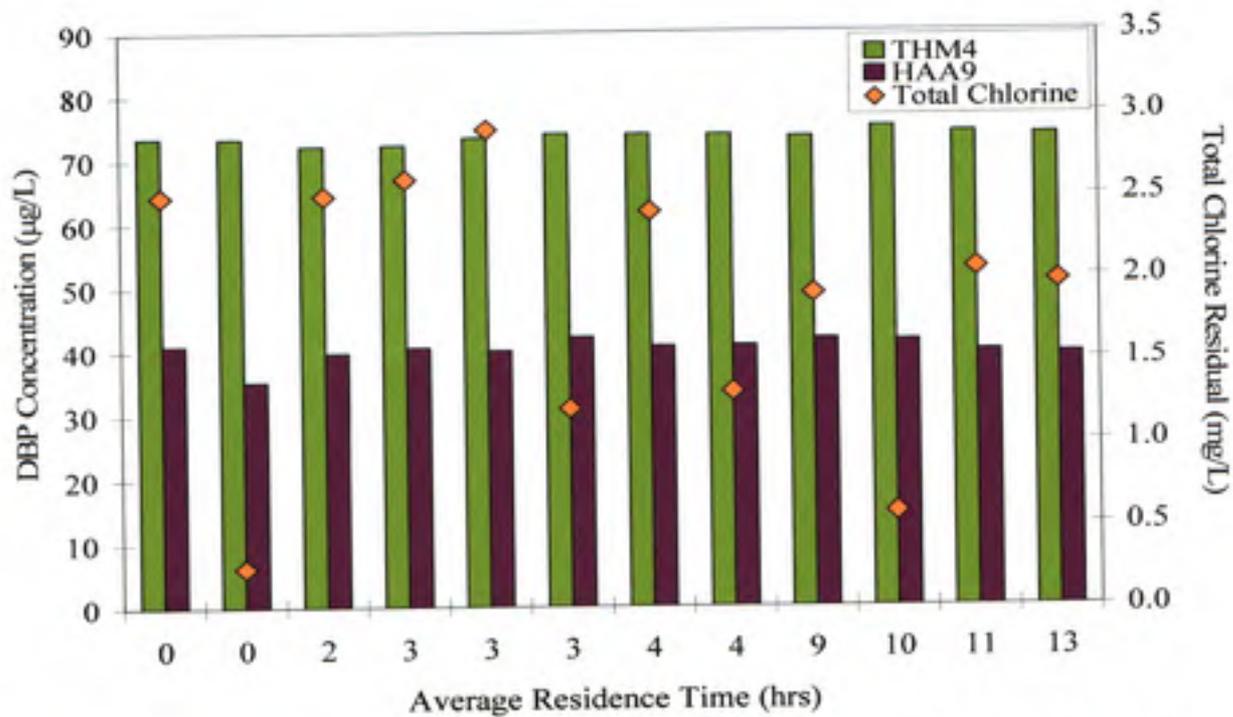


Figure D.19 THM4, HAA9 and total chlorine residual versus average residence time for Utility D for 7/22/03

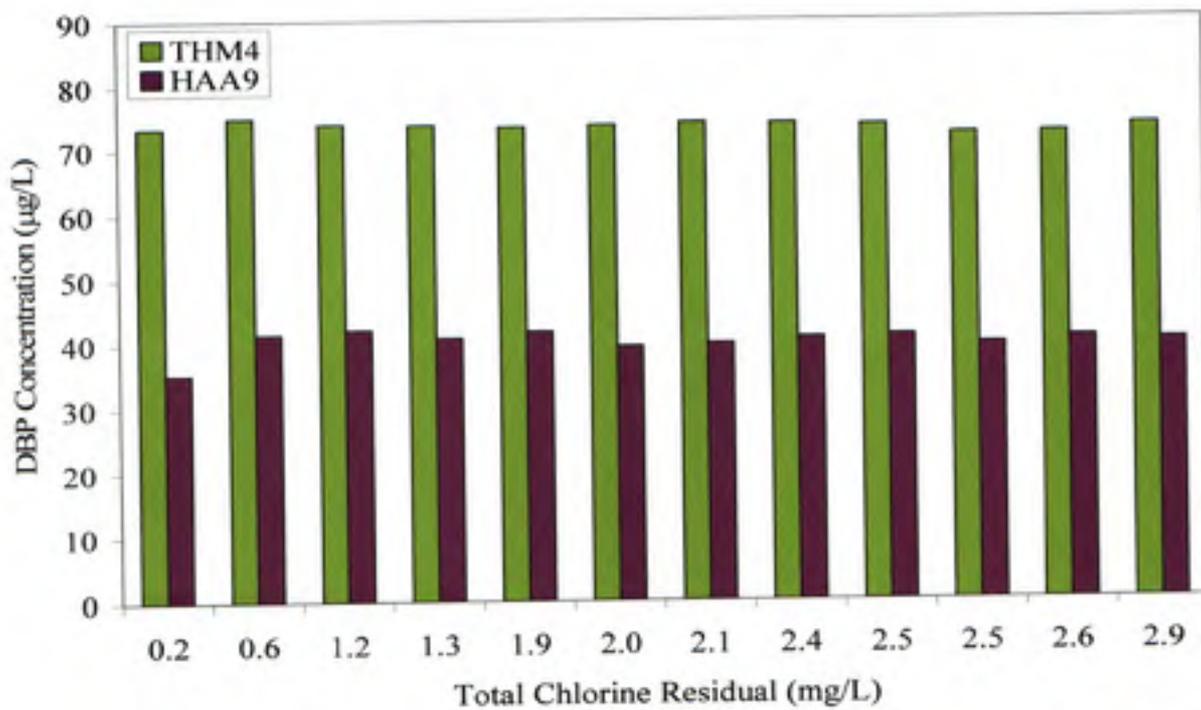


Figure D.20 THM4 and HAA9 concentration versus total chlorine residual for Utility D for 7/22/03

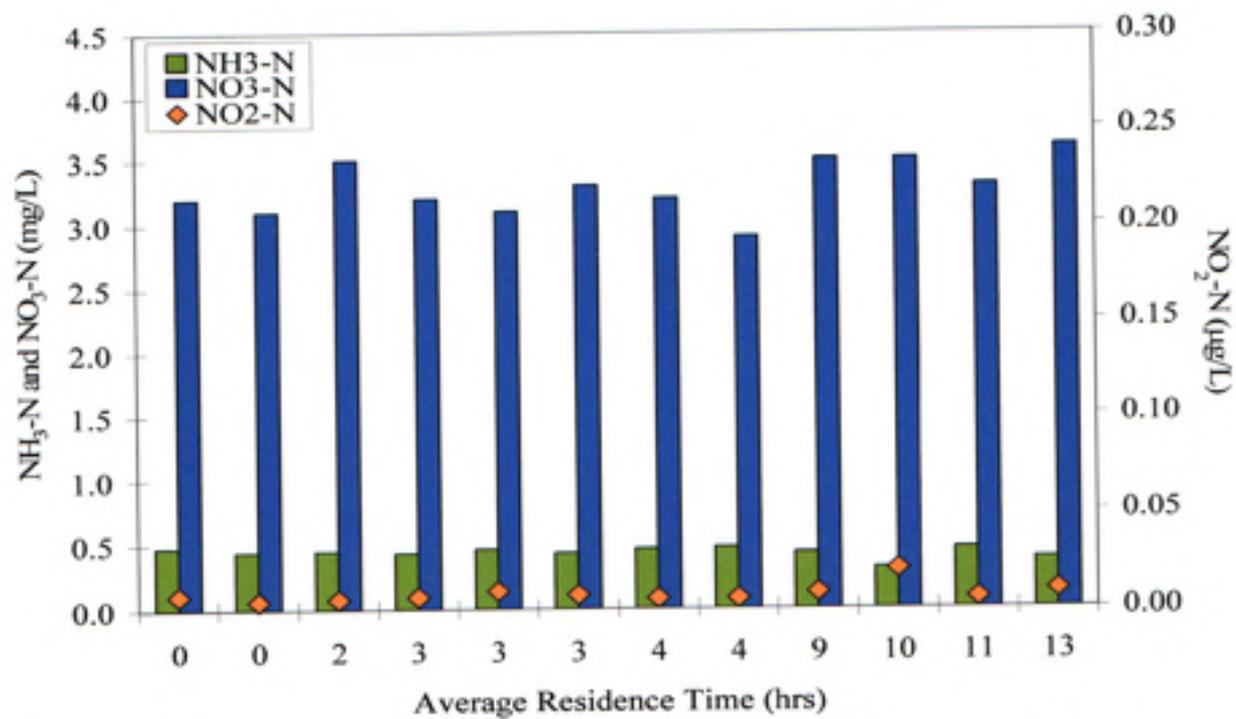


Figure D.21 Nitrogen species versus total chlorine residual for Utility D for 7/22/03

Table D.13

pH, temperature and chlorine data for Utility D for 9/23/03

Sample ID	Temperature		Free Cl <sub>2</sub> (mg/L)	Total Cl <sub>2</sub> (mg/L)
	(°C)	pH		
Site 1	21	8.2	0.21	2.4
Site 2	23	8.1	0.16	3.5
Site 3	22	8.1	0.14	2.3
Site 4	23	8.1	0.18	3.4
Site 5	22	8.1	0.24	2.8
Site 6	22	8.1	0.14	3.3
Site 7	23	8.1	0.12	2.3
Site 8	23	8.2	0.10	2.3
Site 9	21	8.1	0.10	2.4
Site 10	27	8.0	0.24	3.2
Site 12	22	8.1	0.24	2.3
Site 13	27	8.1	0.10	2.2

Table D.14

Organic carbon and microbiological data for Utility D for 9/23/03

Sample ID	AOC (µg/L)	TOC (mg/L)	UV254 (cm <sup>-1</sup> )	HPC (CFU/mL)	NH <sub>3</sub> -N (mg/L)	NO <sub>2</sub> -N (µg/L)	NO <sub>3</sub> -N (mg/L)	Bromide (mg/L)
Site 1	108	2.28	0.049	8.0E+01	0.48	0.006	2.6	0.12
Site 2				1.0E+02	0.46	0.006	2.9	
Site 3				5.0E+01	0.46	0.007	2.9	0.12
Site 4				3.0E+01	0.47	0.005	2.7	
Site 5				4.0E+01	0.4	0.011	2.9	
Site 6				4.0E+01	0.43	0.006	2.9	
Site 7				2.0E+01	0.45	0.008	2.9	0.12
Site 8				1.0E+01	0.46	0.010	2.9	0.12
Site 9				7.9E+02	0.37	0.027	3.0	
Site 10				2.0E+01	0.48	0.006	2.9	0.12
Site 12	81	2.29	0.05	1.0E+01	0.51	0.004	2.9	0.12
Site 13				1.8E+02	0.43	0.006	2.9	0.11

Table D.15

Trihalomethane (THM) data (in µg/L) for Utility D for 9/23/03

Sample ID	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	THM4
Site 1	12	24	36	8	80
Site 2	13	24	37	8	82
Site 3	14	25	39	8	87
Site 4	12	23	36	8	79
Site 5	13	25	38	8	84
Site 6	12	24	36	8	80
Site 7	16	26	40	9	90
Site 8	12	24	36	8	80
Site 9	12	24	36	8	80
Site 10	13	24	37	8	83
Site 12	13	24	37	8	82
Site 13	15	26	40	9	90

Table D.16

Haloacetic acid (HAA) data (in µg/L) for Utility D for 9/23/03

Sample ID	ClAA	BrAA	Cl <sub>2</sub> AA	BrClAA	Br <sub>2</sub> AA	Cl <sub>3</sub> AA	BrCl <sub>2</sub> AA	Br <sub>2</sub> ClAA	Br <sub>3</sub> AA	HAA9
Site 1	<2	<2	7	8	8	4	8	6	4	46
Site 2	<2	<2	6	7	7	4	8	7	4	43
Site 3	<2	<2	7	8	7	5	8	7	4	46
Site 4	<2	<2	7	8	8	5	8	7	4	47
Site 5	<2	<2	6	8	8	5	9	7	4	47
Site 6	<2	<2	7	8	8	5	8	8	4	48
Site 7	<2	<2	7	8	8	5	8	7	4	46
Site 8	<2	<2	7	9	9	5	8	6	4	47
Site 9	<2	<2	7	8	8	5	8	7	4	46
Site 10	<2	<2	6	8	8	5	9	7	4	46
Site 12	<2	<2	6	8	8	5	10	8	4	49
Site 13	<2	<2	7	8	8	5	9	8	4	50

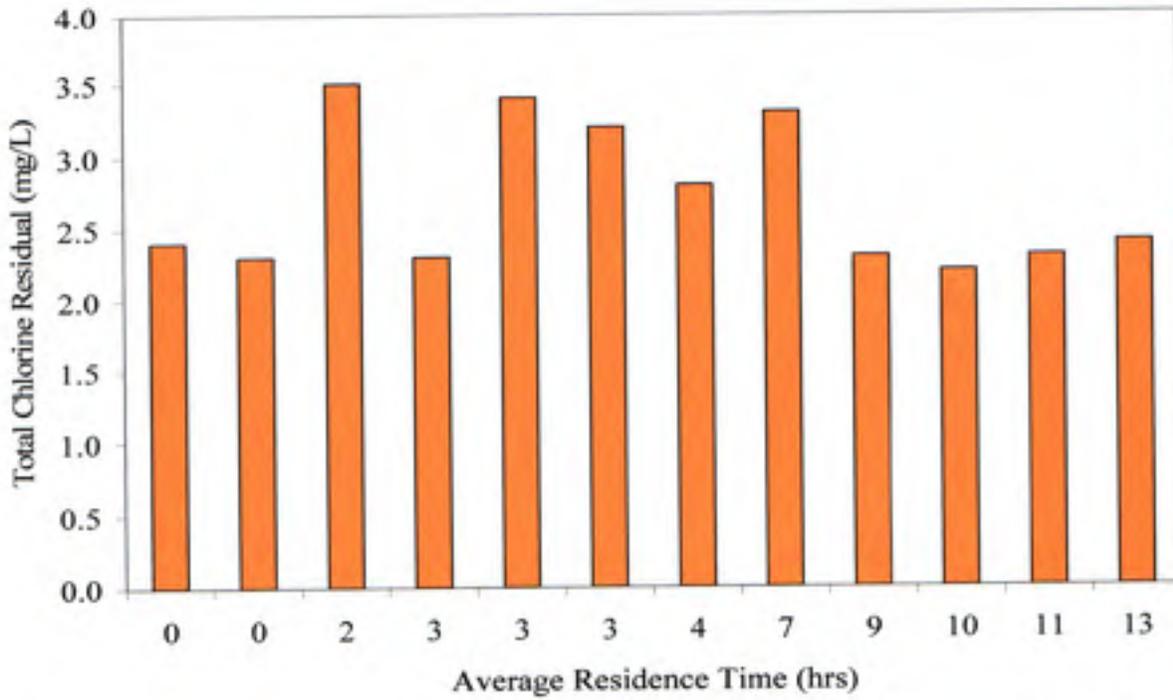


Figure D.22 Total chlorine residual versus average residence time for Utility D for 9/23/03

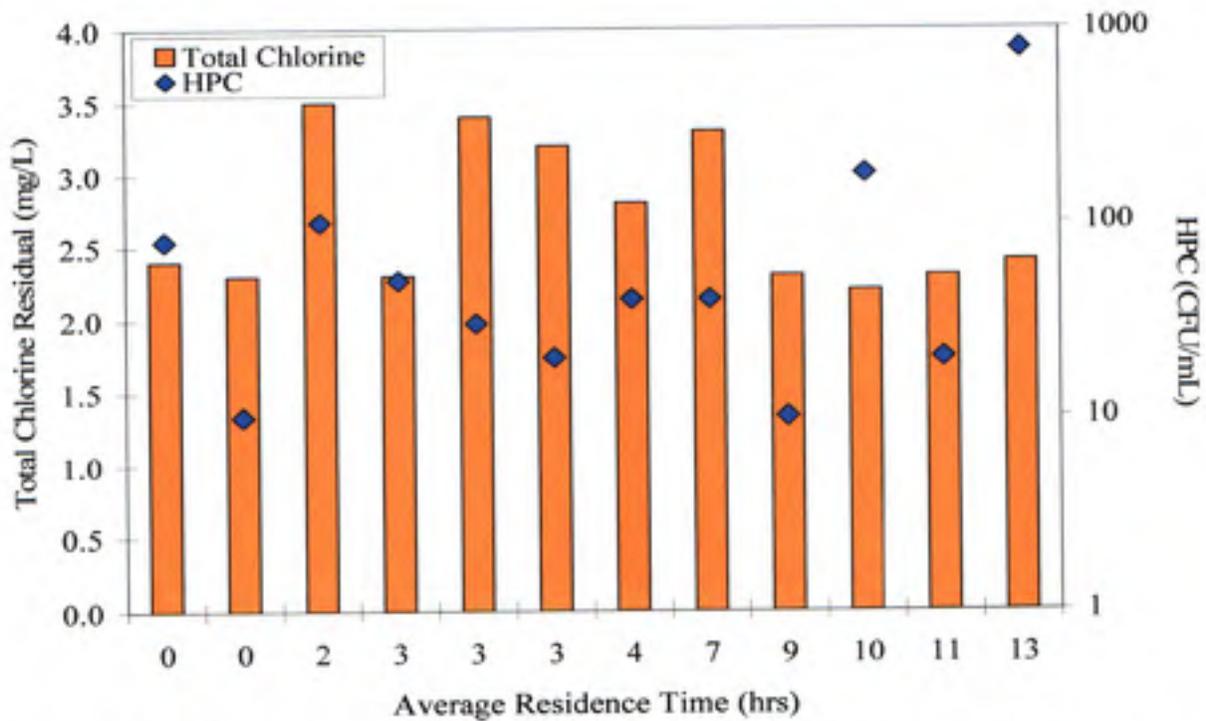


Figure D.23 Total chlorine residual and HPC versus average residence time for Utility D for 9/23/03

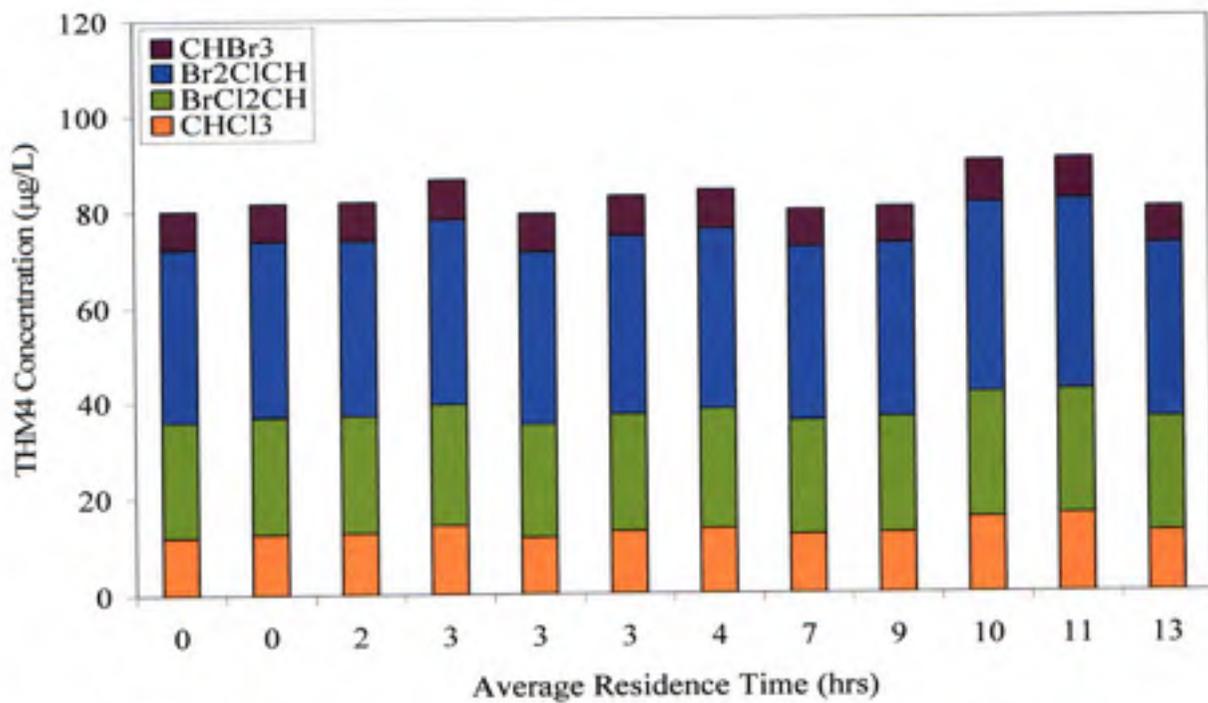


Figure D.24 THM4 speciation versus average residence time for Utility D for 9/23/03

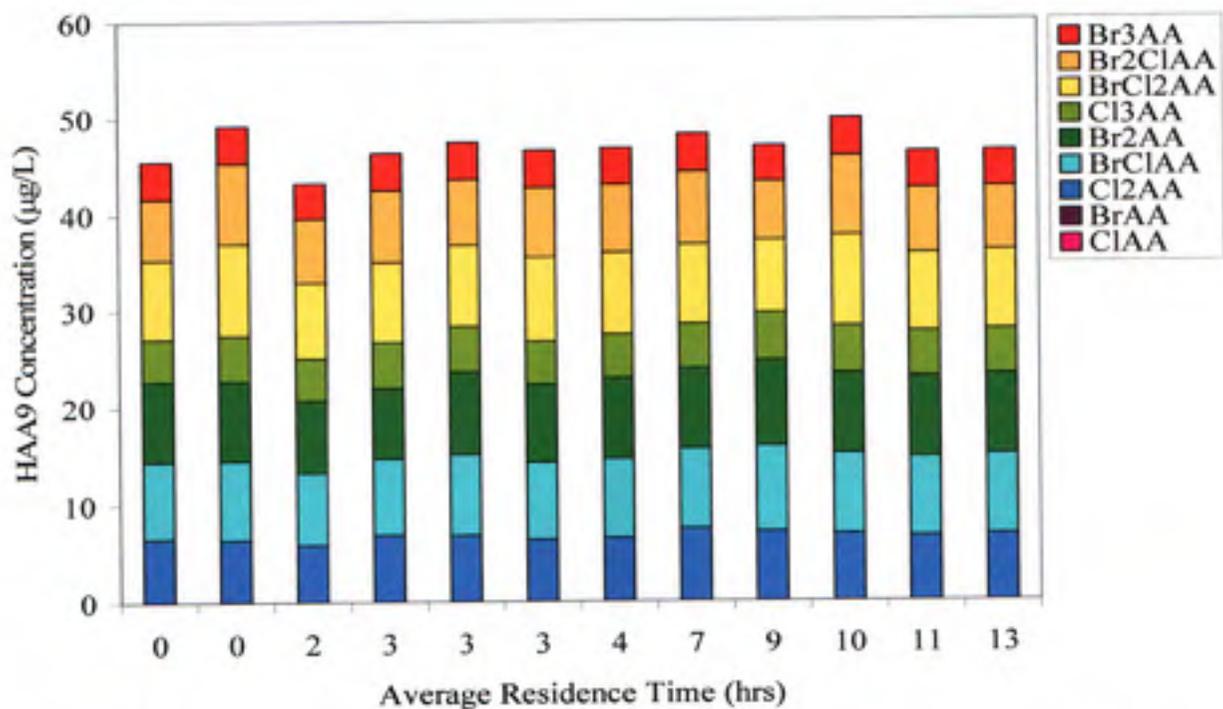


Figure D.25 HAA9 speciation versus average residence time for Utility D for 9/23/03

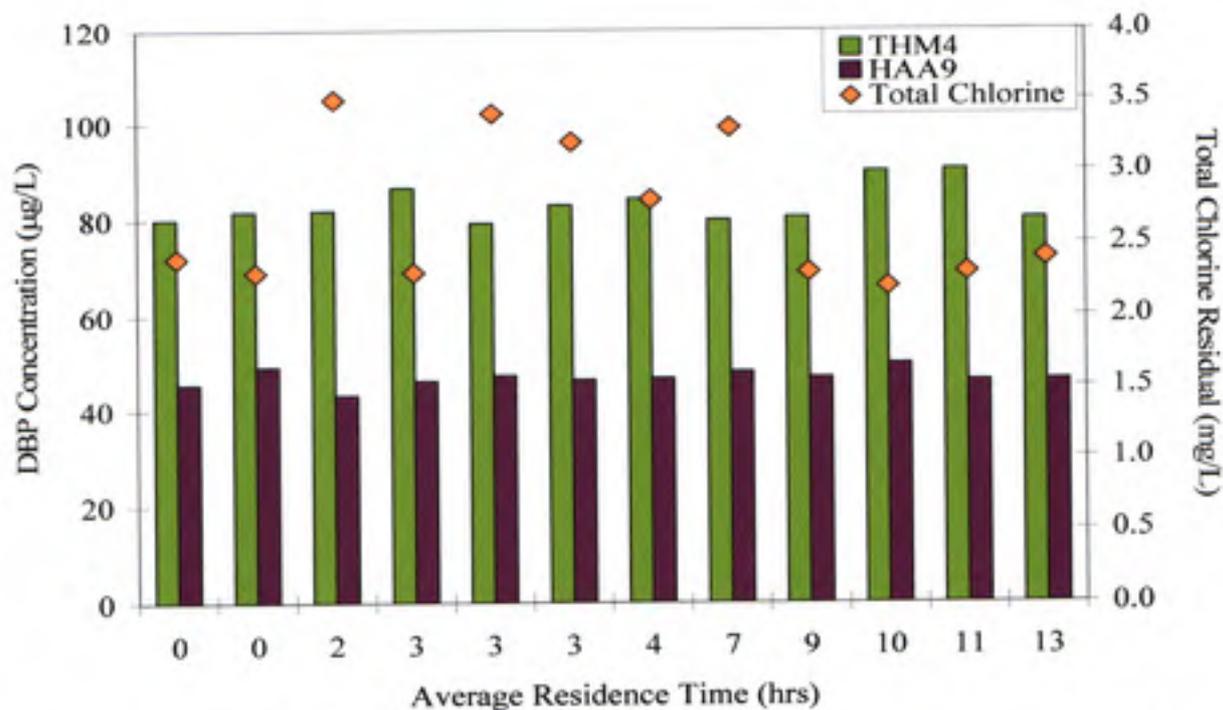


Figure D.26 THM4, HAA9 and total chlorine residual versus average residence time for Utility D for 9/23/03

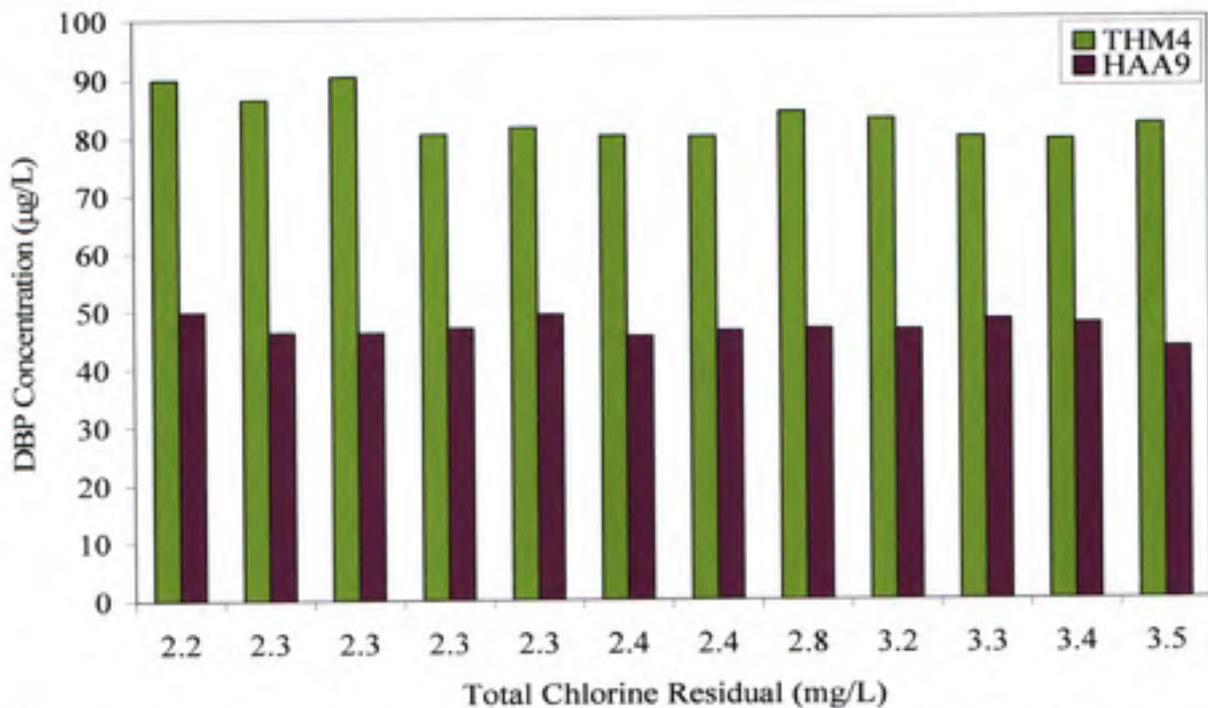


Figure D.27 THM4 and HAA9 concentration versus total chlorine residual for Utility D for 9/23/03

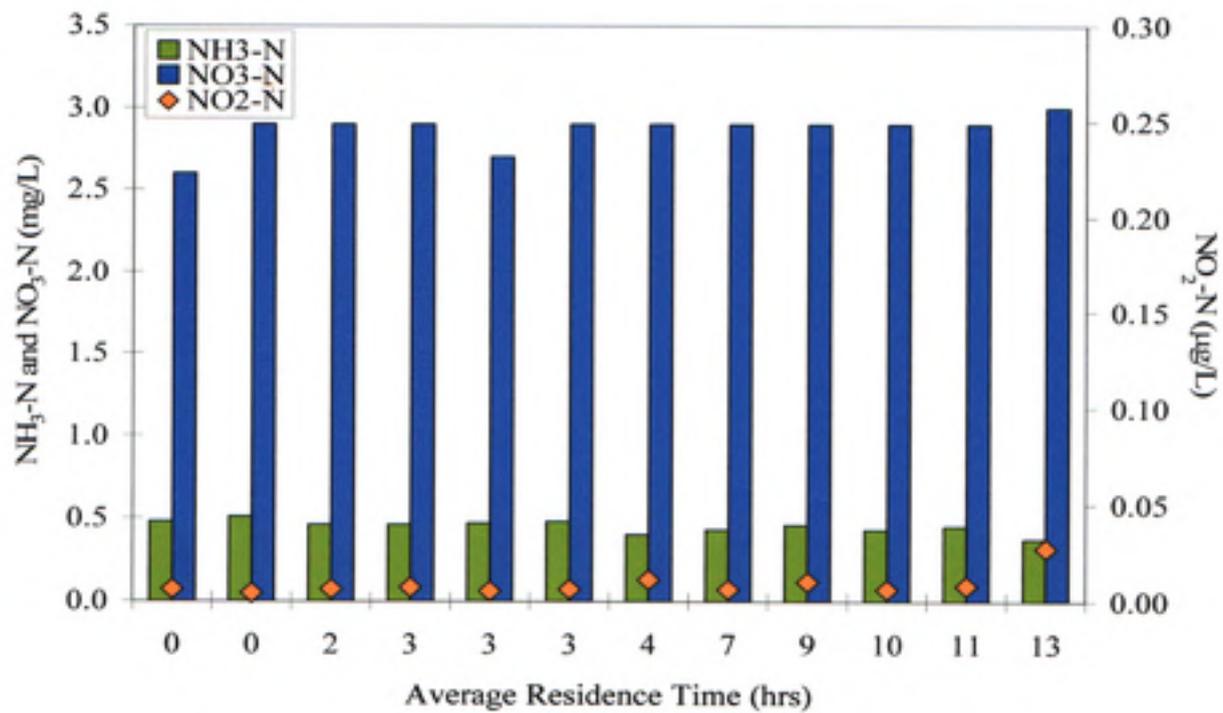


Figure D.28 Nitrogen species versus total chlorine residual for Utility D for 9/23/03