Water Resources Research Institute
of The University of North Carolina

Report No. 430

ASSESSMENT OF NITRIFICATION POTENTIAL AND OCCURANCE IN DRINKING WATER SYSTEMS IN NORTH CAROLINA USING CHLORAMINATION

By
Philip C. Singer, Angella C. Rinehold, and Lauren P. Dunbar

Department of Environmental Sciences and Engineering
Gillings School of Public Health
University of North Carolina at Chapel Hill
Chapel Hill, NC

UNC-WRRI-430

The research on which this report is based was supported by funds provided by the Urban Water Consortium through the Water Resources Research Institute.

This report fulfills the requirements for a project completion report of the Water Resources Research Institute of The University of North Carolina. The authors are solely responsible for the content and completeness of the report.

WRRI Project No. 50370
January 2009

ABSTRACT

Many drinking water utilities are converting from free chlorine to chloramines for secondary disinfection, due in large part to recent promulgation of more stringent regulations governing the allowable concentrations of disinfection byproducts. Although chloramines offer many advantages over free chlorine, chloramine use introduces the potential for nitrification, which can adversely impact water quality in a number of ways. The objective of this study was to assess nitrification potential and occurrence in five chloraminating water systems in North Carolina.

To perform the assessment, historical data were collected from each utility for a period of up to four years. Treatment plant and distribution system data were analyzed for changes in water quality indicative of nitrification. The chlorine-to-ammonia ratios used to form monochloramine were calculated, and the impact of these ratios on the concentration of free ammonia at the point of entry to the distribution system was examined.

Nitrification was evidenced at one of the distribution system sites analyzed. Although the results suggest that each distribution system had sites vulnerable to nitrification, the data necessary to identify nitrification occurrence were not routinely collected by the utilities. The chlorine-to-ammonia ratios were found to vary considerably within and between utilities. The data generally supported the theoretical relationship between increasing chlorine-to-ammonia ratios and decreasing concentrations of free ammonia at the point of entry, suggesting that nitrification potential can be reduced by optimizing the ratio of chlorine to ammonia applied at the point of monochloramine formation. Limited sampling of two of the distribution systems showed that N-nitrosodimethylamine (NDMA), a suspected animal carcinogen, was present at levels below 10 ng/L.

ACKNOWLEDGMENTS

The authors would like to thank the Urban Water Consortium of the North Carolina Water Resources Research Institute for supporting this study, and utility personnel of the Durham Environmental Resources Department, Fayetteville Public Works Commission, Greenville Utilities Commission, Orange Water and Sewer Authority (OWASA), and Raleigh Public Utilities Department who made time in their busy schedules to provide the data necessary to make this research possible. We also thank Dr. Susan Andrews and Ms. Erin Moffat at the University of Waterloo, Ontario, Canada for conducting the NDMA analyses.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1 – INTRODUCTION

Many drinking water utilities across the United States have converted from free chlorine to combined chlorine, or chloramines, for secondary disinfection. Recent surveys indicate that approximately one third of drinking water utilities currently practice chloramination (AWWA and EES 2003; Seidel 2005), and this number is expected to increase in the coming years. While the limited oxidizing and disinfecting power of combined chlorine makes free chlorine the superior choice for primary water treatment, there are a number of advantages to the use of chloramines in the distribution system. Chloramines have been found to help minimize taste and odor problems, improve disinfectant stability, and minimize bacterial regrowth. Perhaps most importantly, chloramines have been found to produce significantly lower levels of regulated disinfection byproducts than free chlorine, namely trihalomethanes (THMs) and haloacetic acids (HAAs). Recent promulgation of Stage 2 of the Disinfectants/Disinfection Byproducts (D/DBP) Rule, which further restricts allowable concentrations of THMs and HAAs compared to previous regulations, has prompted many utilities to convert to combined chlorine.

While combined chlorine offers many advantages over free chlorine, there are a number disadvantages associated with its use. Chloramines have been found to increase the degradation of elastomeric materials common to distribution systems. Also, the comparative stability of chloramines can necessitate more aggressive dechlorination measures prior to certain water uses, such as kidney dialysis or fish rearing. Additionally, there are certain chloramine-related byproducts of concern, most notably cyanogen chloride (CNCl) and *N*-nitrosodimethylamine (NDMA). Lastly, the use of chloramines introduces the potential for nitrification.

Nitrification is the process by which ammonia is sequentially oxidized to nitrite and then to nitrate by nitrifying bacteria. As ammonia is introduced into the distribution system from chloramine formation and decay, these microorganisms can proliferate and adversely impact water quality in a number of ways. Nitrification can lead to the accelerated loss of chloramine residual, increased bacterial regrowth and coliform occurrence, increased corrosivity, and increased nitrite and/or nitrate concentration. The potential impacts of nitrification can be severe, and its occurrence is pervasive among utilities using chloramines. Surveys have shown that as many as two thirds of chloraminating utilities have experienced nitrification (Wilczak et al. 1996).

There are a number of water quality and distribution system characteristics that impact a utility's vulnerability to nitrification. Nitrifying activity is highly dependent upon the concentration of free ammonia entering the distribution system from the treatment plant, which is a function of the chlorine-to-ammonia ratio used to form monochloramine. It is also dependent upon finished-water temperature, pH, disinfectant residual, and natural organic matter (NOM) concentration. Distribution system pipe material, hydraulic residence time, and the presence of sediments and biofilms are also important factors in nitrification occurrence.

Nitrification is typically marked by significant losses in disinfectant residual, increases in nitrite and/or nitrate concentration, and decreases in total ammonia concentration. Increased heterotrophic plate counts (HPC) may also be detected during episodes of nitrification. Nitrification also causes decreases in pH, alkalinity, and dissolved oxygen (DO) concentration, although unrelated reactions in the distribution system can mask the effects of nitrification on these parameters.
The objectives of this study were to assess the degree to which each of the five members of the North Carolina Urban Water Consortium using chloramines have experienced symptoms of

nitrification in recent years, and to evaluate treatment plant operating practices and finished-water quality characteristics that may influence nitrification potential. Historical data were collected from each utility's water treatment plant(s) and distribution system, and these data were analyzed to identify the changes in water quality indicative of nitrification. The parameters assessed for change between the treatment plant and the distribution system included disinfectant residual, nitrite, nitrate, ammonia, pH, HPC, and DO. In addition to assessment of the changes, the finished-water free ammonia concentrations, pH values, and total organic carbon (TOC) concentrations were evaluated. The data were also analyzed to determine the chlorine-to-ammonia ratios used to form monochloramine, as well as the length and consistency of temporary conversions from chloramines to free chlorine. The results of these analyses were compared to standard practices and recommendations.

In addition, selected samples were analyzed for N-nitrosodimethlamine (NDMA), a suspected animal carcinogen found to occur in chloraminated drinking waters.

CHAPTER 2 – LITERATURE REVIEW

2.1 SECONDARY DISINFECTION WITH CHLORAMINES

Free chlorine and chloramines, or combined chlorine, have been used for disinfection of drinking water in the United States since the early 1900s. Due to its greater disinfecting power and ability to rapidly inactivate microbes, free chlorine is the superior primary disinfectant. While free chlorine has also traditionally been the secondary disinfectant of choice for most utilities, the use of chloramines in distribution systems is on the rise. A survey by Wilczak et al. (1996) revealed that 22% of utilities were using chloramines for secondary disinfection in 1990. Chloramine use steadily increased in subsequent years, and more recent surveys found that 29-33% of utilities were practicing chloramination (AWWA and EES 2003; Seidel 2005). This number is expected to increase further, and it has been predicted that chloramines will be employed by up to 65% of surface water systems (AWWA and EES 2003).

There are a number of aesthetic and regulatory drivers behind this shift from free chlorine to chloramines. Many utilities have experienced fewer taste and odor (T&O) problems with the use of chloramines (Kirmeyer et al. 2004; Neden et al. 1992). Chloraminated water typically has a less chlorinous T&O than chlorinated water, and the efficacy of chloramines against bacterial regrowth helps to prevent bacteria-related T&O problems. This effectiveness at preventing bacterial regrowth has also allowed for better control of coliform bacteria with chloramines than free chlorine (Kirmeyer et al. 2004; LeChevallier et al. 1996; Neden et al. 1992; Norton and LeChevallier 1997), and hence better compliance with the Total Coliform Rule (TCR). Additionally, the stability of chloramines relative to free chlorine has helped utilities maintain a more consistent disinfectant residual throughout the distribution system (Kirmeyer et al. 2004; Neden et al. 1992), and thus better comply with the residual maintenance requirements of the Surface Water Treatment Rule (SWTR). Finally, many utilities are finding it necessary to convert to chloramines in order to meet the requirements of the recently-promulgated Stage 2 of the Disinfectants/Disinfection Byproducts (D/DBP) Rule, which further restricts allowable concentrations of trihalomethanes (THMs) and haloacetic acids (HAAs) compared to previous regulations. Data show 40-80% reductions in the formation of THMs with chloramines relative to free chlorine (Kirmeyer et al. 2004), and available data on the production of HAAs also suggest reduced formation with chloramines (Kirmeyer et al. 2004; Norton and LeChevallier 1997). These potential improvements in water quality are prompting increasing numbers of utilities to employ chloramines for secondary disinfection.

2.1.1 Chemistry of Chloramine Formation

In aqueous solutions, free chlorine ($HOCl$) readily reacts with ammonia (NH_3) to form inorganic chloramines, namely monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine, or nitrogen trichloride (NCl_3).

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \tag{2.1}$$
$$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O \tag{2.2}$$
$$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O \tag{2.3}$$

A number of factors influence which of the above reactions dominates. Chloramine speciation is dependent upon pH, the ratio of free chlorine to ammonia-N (Cl_2:NH_3-N), temperature, and contact time. Monochloramine is the preferred chloramines species for disinfection due to its biocidal properties, stability, and less chlorinous taste and odor, and it is the predominant species formed under typical drinking water conditions. Optimum conditions for monochloramine formation are pH 8.3 to 8.4, 25°C, and a Cl_2:NH_3-N weight ratio (mg Cl_2:mg NH_3-N) of 4:1 to 5:1 (Kirmeyer et al. 2004). Under these conditions, monochloramine forms in a few seconds or less. This rate of formation is highly dependent upon temperature. A reduction in temperature from 25 to 0°C has been shown to increase the formation time from 0.2 seconds to five minutes (White 1999). Optimum conditions for dichloramine formation are pH 4 to 6 and Cl_2:NH_3-N weight ratios of 5:1 to 7:1 (Kirmeyer et al. 2004), and significant quantities of trichloramine are typically not present unless pH values are less than 4 (Snoeyink and Jenkins 1980).

The 1:1 Cl_2:NH_3-N molar ratio involved in monochloramine formation (Reaction *2.1*) is equivalent to approximately a 5:1 Cl_2:NH_3-N weight ratio. At weight ratios less than 5:1, all free chlorine is consumed and excess free ammonia will exist in solution. At weight ratios greater than 5:1, excess free chlorine will react to destroy the total chlorine (sum of free and combined chlorine) concentration. At weight ratios approaching 7.6:1 (molar ratios of 1.5:1), the total chlorine concentration will decrease to zero or near zero through a complex set of reactions known as the breakpoint reactions, which are not entirely understood. This loss of total chlorine proceeds through the formation and subsequent decomposition of dichloramine to form nitrogen-containing products, including nitrogen gas, nitrate, nitrous oxide, and nitric oxide (Kirmeyer et al. 2004). The overall stoichiometry of the formation and subsequent destruction of chloramines is shown by

$$3\ HOCl + 2\ NH_3 \rightarrow N_{2(g)} + 3\ H^+ + 3\ Cl^- + 3\ H_2O \qquad (2.4)$$

The Cl_2:NH_3-N ratio at which the complete oxidation of ammonia occurs is known as the breakpoint. Beyond this point, the total chlorine residual will increase with the free chlorine dose at a ratio of 1:1, and all free chlorine dosed will remain as free chlorine. As shown by Reaction *2.4*, the theoretical breakpoint is 1.5:1 on a molar basis or 7.6:1 on a weight basis. However, actual breakpoint ratios are typically higher and are a function of temperature, pH, and the oxidant demand of the water. Kirmeyer et al. (2004) report observations of breakpoint weight ratios ranging from 10:1 to 12.5:1 at pH values between 6 and 9. Thus, the actual breakpoint ratio is specific to each water.

In addition to reacting with ammonia to form inorganic chloramines, chlorine can also react with a variety of nitrogenous organic compounds to form organic chloramines. Wolfe et al. (1985) found that free chlorine can preferentially react with these nitrogenous organic compounds, which results in decreased disinfection potential, as organic chloramines have little or no biocidal activity. Further, long residence times can result in the conversion of inorganic to organic chloramines (Wolfe et al. 1985). The presence of organic chloramines is problematic because conventional techniques used to measure chloramine residual cannot distinguish between organic and inorganic species (Wolfe et al. 1985), thus making it difficult to accurately gauge the disinfecting power of a water.

2.1.2 Chloramine Demand and Decay

Though monochloramine is relatively stable compared to free chlorine, it will react with a number of bulk water and pipe wall constituents, such as natural organic matter (NOM), nitrite, and ferrous iron. Even in the absence of such reducing agents, monochloramine will autodecompose over time.

Excessive loss of chloramine residual by demand and decay reactions can lead to insufficient protection against microbes. Furthermore, chloramine decay results in the release of free ammonia, which can make the distribution system vulnerable to nitrification (see Section 2.2).

Monochloramine autodecomposes through the formation and subsequent decomposition of dichloramine. Given that dichloramine is much less stable than monochloramine under typical drinking water conditions (Diehl et al. 2000), the formation of dichloramine is the rate-limiting step in monochloramine decay (Harrington et al. 2003). There are two major pathways that lead to the formation of dichloramine: 1) the hydrolysis of monochloramine to form free chlorine (Reaction *2.1* in reverse), followed by the formation of dichloramine (Reaction *2.2*); and 2) the acid-catalyzed disproportionation of monochloramine to dichloramine, as shown below (Valentine and Jafvert 1988; Wilczak et al. 2003):

$$2\ NH_2Cl + H^+ \rightarrow NH_4^+ + NHCl_2 \qquad (2.5)$$

The net autodecomposition of monochloramine can be characterized as follows (Vikesland et al. 1998):

$$3\ NH_2Cl \rightarrow N_{2(g)} + NH_3 + 3\ H^+ + 3\ Cl^- \qquad (2.6)$$

Generally speaking, the rate of chloramine decay by autodecomposition is slower than that of chlorine (Valentine et al. 2000; Westbrook 2006). The specific rate of decay is highly dependent upon a number of factors, including temperature, pH, the initial chloramine concentration, and the Cl_2:NH_3-N ratio. Monochloramine is significantly more stable at lower temperatures and higher pH values. Valentine et al. (1998) observed a 6.5-fold increase in the rate of decay by increasing the temperature from 4 to 35°C, as well as a decrease in half-life from approximately 300 hours to 40 hours by reducing the pH from 7.5 to 6.5. Vikesland et al. (2001) also observed the trend of increasing decay rates with decreasing pH values, which was attributed to the enhanced rate of dichloramine formation associated with lower pH values. Valentine et al. (1998) found faster decay rates to be associated with higher initial chloramine concentrations. Theoretically, higher Cl_2:NH_3-N ratios (and thus lower free ammonia concentrations) should also result in more rapid autodecomposition. Indeed, experiments by Vikesland et al. (1998) indicate that high free ammonia concentrations can slow the rate of chloramine decay. However, the high ammonia concentrations used in these experiments (14 and 140 mg/L) are well outside the range of values typically found in drinking water. In practice, the range of ammonia concentrations likely to be found in drinking water should have no significant effect on the rate of chloramine decay (Harrington et al. 2003). Furthermore, Valentine et al. (1998) found that the effect of the Cl_2:NH_3-N ratio became less important at higher pH values. At a pH value of 8.3, varying the ratio did not change the rate of chloramine decay.

Another pathway for loss of chloramine residual is the oxidation of NOM. Although the reaction mechanism between monochloramine and NOM has not been well studied, it is generally accepted that the presence of NOM accelerates chloramine decay. Vikesland et al. (1998) performed experiments to determine whether the loss in chloramine residual associated with NOM is the result of a direct reaction between monochloramine and NOM, or rather a catalytic reaction between NOM and the mechanisms driving autodecomposition. The results of these experiments suggest that NOM acts as a direct reducing agent rather than a catalyst. If the chemical composition of

NOM is assumed to be $C_5H_7O_2N$, the following expression describes the oxidation of NOM by monochloramine (Woolschlager et al. 2001b):

$$1/10\ C_5H_7O_2N + NH_2Cl + 9/10\ H_2O \rightarrow 4/10\ CO_2 + 1/10\ HCO_3^- + 11/10\ NH_4^+ + Cl^- \quad \textit{(2.7)}$$

This reaction follows dual-phase kinetics (Valentine et al. 1998), which involves an initial rapid loss of chloramine residual, followed by a slow but appreciable loss in residual (Valentine et al. 2000). It has been reported that oxidation reactions with NOM are the dominant source of chloramine decay during the first 24 to 36 hours following chloramine formation, at which point autodecomposition begins to govern the decay rate (Bone et al. 1999, Harrington et al. 2003).

The presence of reduced (ferrous) iron can also exert a significant chloramine demand. Although iron originating in the source water is generally oxidized and removed during the treatment process, reduced forms of iron can be generated in the distribution system by corrosion reactions. Despite practices aimed at controlling corrosion, such as the use of corrosion inhibitors and pH adjustment, corrosion continues to be a concern for many utilities. Reactions between chloramine and ferrous iron can take place in the bulk water or at the surface of iron pipes. A study by Vikesland and Valentine (2000) confirmed that the direct reaction between monochloramine and ferrous iron is dominant compared to the indirect reaction involving the hydrolysis of monochloramine and subsequent oxidation of ferrous iron by free chlorine. The study also indicated that the oxidation of ferrous iron is autocatalytic; oxidation occurs in the bulk solution, as well as at the surface of the ferric oxide precipitate produced by the reaction in the bulk solution. Prior to experiments, the authors predicted that the following reaction would characterize the oxidation of ferrous iron by monochloramine:

$$2\ Fe^{+2} + NH_2Cl + 6\ H_2O \rightarrow 2\ Fe(OH)_{3(s)} + NH_3 + Cl^- + 5\ H^+ \qquad \textit{(2.8)}$$

Results of the study indicated, however, that the reaction is quite complex and that the stoichiometry is not exactly 2:1 Fe(II):NH_2Cl as suggested by Reaction *2.8*. While the reaction mechanisms are not yet well understood, it is clear that the chloramine demand exerted by ferrous iron can be significant. Although chloramines have been found to be less reactive with reduced iron than free chlorine (Valentine et al. 2000), exposure to corrosion products has been linked to appreciable chloramine loss. Recent research by Westbrook (2006) indicates that unlined cast iron pipes can exert a significant chloramine demand, resulting in a chloramine reaction rate one order of magnitude higher than that associated with cement-lined iron pipes.

Nitrite will also exert a chloramine demand. While nitrite introduced into the distribution system from the source water is typically minimal, significant concentrations of nitrite can be produced by partial nitrification (see Section 2.2). As with the oxidation of ferrous iron, the direct reaction between nitrite and monochloramine has been shown to dominate relative to the oxidation of nitrite by free chlorine generated by monochloramine hydrolysis (Margerum et al. 1994). The net oxidation reaction is typically characterized as follows:

$$NH_2Cl + NO_2^- + H_2O \rightarrow NH_4^+ + NO_3^- + Cl^- \qquad \textit{(2.9)}$$

Research by Margerum et al. (1994) found free chlorine to be approximately 1.8×10^5 times more reactive with nitrite than monochloramine. Despite the relatively slow kinetics of the reaction between nitrite and monochloramine, the presence of nitrite has been associated with rapid and severe reductions in chloramine residual. Woolschlager et al. (2001b) have suggested that the accelerated loss of chloramine residual observed during periods of elevated nitrite concentration is too great to be explained by the oxidant demand exerted by nitrite. Instead, they proposed that the relationship between elevated nitrite concentration and chloramine loss may be due to the presence of ammonia-oxidizing bacteria (AOB) that is implied by an increase in nitrite concentration. The authors proposed that AOB act to cometabolize monochloramine. While little research has been done to examine the possible cometabolism of monochloramine by AOB, Woolschlager et al. (2001b) found that their model best predicted distribution system data when the cometabolic reaction was included. Further, this proposed mechanism of chloramine decay is consistent with experimental findings by Hao et al. (1994), namely that the stoichiometry of the disappearance of monochloramine and nitrite is not 1:1, as suggested by Reaction *2.9*. Therefore, chloramine decay may be attributable to biological reactions associated with the presence of nitrite in addition to a direct chemical reaction between monochloramine and nitrite.

Again, each of the four pathways of chemical chloramine decay described above results in the release of free ammonia. The oxidant demands exerted by NOM, ferrous iron, and nitrite lead to the release of ammonia at a molar ratio at or near 1:1 NH_2Cl:NH_3. For autodecomposition, the molar ratio is 3:1 NH_2Cl:NH_3. The release of ammonia from these demand and decay mechanisms can adversely affect water quality by fueling nitrification, as described in Section 2.2.

2.1.3 Disinfection Efficacy

The superior disinfecting power of free chlorine relative to chloramines against free, or unattached, bacteria has been well documented. Griebe et al. (1993) found that exposure to 2 mg/L of monochloramine for 15 minutes resulted in 2-log inactivation of free bacteria. When the bacteria were exposed to 1 to 2 mg/L of free chlorine, 100% inactivation was achieved within two minutes. LeChevallier et al. (1988) report that 2-log inactivation of unattached bacteria was achieved by exposure to 0.08 mg/L of free chlorine for one minute, whereas the same degree of inactivation by monochloramine required exposure at 94 mg/L for one minute. This finding that free chlorine is approximately 1200 times more effective at inactivating free bacteria is consistent with results found by other investigators.

The disinfection efficacy of monochloramine against bacteria associated with biofilms is also an important consideration, as most of the microorganisms in waterworks systems are associated with surfaces (Griebe et al. 1993). A biofilm consists of microbial cells embedded in a matrix of extracellular polymeric material attached to a substratum, such as a pipe wall. Biofilms can protect embedded microbes from disinfection by providing a diffusional barrier as well as a source of disinfectant demand. Because monochloramine is more selective than free chlorine in the types of compounds with which it will react (LeChevallier et al. 1990), it is less likely to be consumed by exopolysaccharide material typically found in biofilms and may therefore penetrate deeper into biofilms to inactivate microbes (Koudjonou et al. 1998). A study by Chen and Stewart (1996) found that free chlorine can be neutralized by reactions with biofilm constituents faster than it can diffuse into the biofilm, thereby corroborating findings that biofilm oxidant demand may significantly impair the biocidal efficacy of free chlorine.

The surface to which biofilms are attached can also impact the penetrative capacity of a disinfectant. Numerous researchers (Ferguson 2005; LeChevallier et al. 1990) have found biocides to be less effective at inactivating biofilms growing on iron pipe than on other substrata, such as copper or polyvinyl chloride (PVC). As indicated above, corrosion products associated with iron pipes can exert a significant disinfectant demand, particularly for free chlorine. The greater reactivity of free chlorine is attributed, in part, to its higher oxidation potential and its ability to break up iron complexes in order to access and oxidize ferrous iron (White 1986). LeChevallier et al. (1993) found that low levels of corrosion could interfere with the disinfection by free chlorine of biofilms on iron pipe, whereas higher corrosion rates were required to interfere with the efficacy of monochloramine. Thus, the relatively high free-chlorine demand exerted by biofilms and the substrata to which they are attached can make chloramines more effective at inactivation of attached bacteria. Furthermore, the lower reactivity of chloramines with reducing agents common to distribution systems can result in a more persistent disinfectant residual, which has important implications in the protection against bacterial regrowth.

The degree to which the oxidant demand exerted by biofilms and their substrata impacts the disinfection efficacy of free chlorine and chloramines has been well studied. In experiments conducted on iron pipes, LeChevallier et al. (1990) found that the exposure of biofilm bacteria to a free chlorine dose of 4 mg/L (3 mg/L residual) for two weeks did not show significant changes in cell viability, while exposure to 4 mg/L of monochloramine for the same period of time resulted in over 3-log inactivation. Griebe et al. (1993) observed that exposure of attached bacteria to 4 mg/L of monochloramine resulted in a viable cell reduction of four orders of magnitude after one hour, while exposure to 10.8 mg/L of free chlorine for one hour resulted in a viable cell reduction of only three orders of magnitude. The ability of chloramines to better inactivate attached bacteria has prompted utilities using free chlorine to convert to chloramines in an effort to control biofilm-related bacteria, most notably coliforms. This change in secondary disinfection has met with considerable success. Norton and LeChevallier (1997) report that a chlorinating utility was coliform positive in nearly 25% of all samples prior to the conversion to chloramines. Within one week of conversion, all samples were negative for coliform and the system remained coliform-free for years. Numerous other studies have also reported fewer coliform occurrences and reduced numbers of heterotrophic bacteria with chloramines compared to free chlorine (Kirmeyer et al. 2004; LeChevallier et al. 1996; Neden et al. 1992). Thus, despite the stronger disinfecting power of free chlorine, chloramines may be the more effective biocide under certain water quality and distribution system conditions.

2.1.4 Disadvantages of Chloramination

While the advantages of chloramination can make it an attractive alternative to the use of free chlorine, there are a number of disadvantages associated with chloramine use. Chloramines are considerably more aggressive than free chlorine against elastomeric materials, such as those found in distribution system plumbing (Reiber 1993). Recent surveys indicate that 16-23% of chloraminating utilities have experienced problems with elastomer cracking, swelling, or decay (Kirmeyer et al. 2004; Seidel 2005). Additionally, the comparative stability of chloramines can necessitate more aggressive dechlorination measures prior to certain water uses, such as kidney dialysis or fish rearing. Chloramine residual persistence can also exacerbate damage caused by accidental releases to the environment, as evidenced by widespread fish kills resulting from leaks in a chloraminated distribution system in British Columbia (Neden et al. 1992). Also, although chloramines have been found to reduce the formation of THMs and HAAs, there are certain chloramine-related byproducts of potential concern. The most noteworthy of these byproducts are cyanogen chloride (CNCl) and *N*-nitrosodimethylamine (NDMA). CNCl formation during chloramination is of growing concern, and the compound was added to the list of contaminants to be monitored under the Information Collection Rule (USEPA 1996). NDMA has been classified by the U.S. Environmental Protection Agency (USEPA) as a probable human carcinogen, though its presence in drinking water is not currently federally regulated. Studies have shown that CNCl is formed in greater amounts and is more stable during chloramination than chlorination (Krasner et al. 1989), and that NDMA only forms in chloraminated water (Choi and Valentine 2002). Finally, and perhaps most notably, the use of chloramines as a secondary disinfectant introduces the potential for nitrification, a microbiological process that can adversely impact water quality as described in the following sections.

2.2 NITRIFICATION IN DISTRIBUTION SYSTEMS

Among the most serious drawbacks to the use of chloramines for secondary disinfection is the potential for nitrification in distribution systems. Nitrification is the two-step microbial process by which ammonia is sequentially oxidized to nitrite (NO_2^-) and then to nitrate (NO_3^-). The first step in this two-part process, known as partial nitrification, is carried out by ammonia-oxidizing bacteria (AOB):

$$NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+ \qquad (2.10)$$

Complete nitrification occurs when the second step is then carried out by nitrite-oxidizing bacteria (NOB):

$$NO_2^- + 1/2\ O_2 \rightarrow NO_3^- \qquad (2.11)$$

The autotrophic bacteria most frequently identified with the oxidation of ammonia and nitrite are *Nitrosomonas* and *Nitrobacter*, respectively, although other genera can also carry out these biochemical reactions (Watson et al. 1989). More recent research has identified *Nitrospira* as the predominant nitrite-oxidizing bacteria genus (Regan et al. 2002; Regan et al. 2003). While research has confirmed the ubiquitous presence of AOB (Regan et al. 2003; Wolfe et al. 1990) and NOB (Regan et al. 2002) in chloraminating systems, operating conditions are typically sufficient to suppress their activity. However, potential increases in ammonia concentration from chloramine formation and decay make the systems vulnerable to nitrification. If distribution system conditions shift to favor the growth of nitrifying bacteria, the microorganisms can proliferate and impact water quality in a number of ways, including accelerated loss of chloramine residual, increased coliform occurrences, increased corrosivity, and increased nitrite and/or nitrate concentrations. The adverse impacts of nitrification can be severe, and its occurrence is pervasive among utilities using chloramines. An estimated two thirds of chloraminating utilities surveyed by Wilczak et al. (1996) experienced nitrification to some degree, and approximately one in four utilities reported moderate to severe nitrification problems.

2.2.1 Optimal Conditions for Occurrence

Although nitrifying activity can occur under a wide variety of conditions, certain factors have consistently been linked to episodes of nitrification. Two such factors are high free ammonia concentration and low chloramine residual. Because AOB utilize ammonia as a growth substrate, the availability of ammonia is requisite to nitrifying activity. The presence of ammonia in the distribution system can result from excessive ammonia dosage at the treatment plant during chloramine formation, or from ammonia release by chloramine decomposition (see Sections 2.1.1 and 2.1.2). Although introduction of free ammonia directly from the treatment plant certainly favors nitrification, it has been shown that AOB can survive when there is no available ammonia except that which is released by chloramine decay (Harrington et al. 2003). Low chloramine residual is also critical to the growth of AOB and NOB. Although nitrification has been reported at chloramine concentrations as high as 4.6 mg/L (Skadsen 1993), the likelihood of occurrence increases considerably as disinfectant residual decreases. In a study by Harrington et al. (2002), nitrification episodes occurred only after the disinfectant residual reached concentrations of 1.1 mg/L or less.

Long hydraulic residence time (HRT), typically associated with low-flow or dead-end regions of the pipe network and with storage tanks and reservoirs, can contribute to nitrification in a number of ways. AOB and NOB are relatively slow-growing organisms (Wood 1986), and appreciable HRT is required for their growth in the bulk solution. Long HRT can also allow nitrifying bacteria time to acclimate to system conditions, such as pH and biocide concentration. Additionally, long residence time contributes to bacterial growth by providing time for the chloramine residual to dissipate by reactions with reducing substances in the system and by autodecomposition. As these decomposition reactions proceed through the distribution system and release ammonia, the agent responsible for controlling AOB growth disappears while the agent responsible for fueling AOB growth accrues. Therefore, it is not surprising that a positive correlation between HRT and nitrification occurrence is well documented (Cunliffe 1991; LeChevallier et al. 1987; Skadsen 1993; Wolfe et al. 1988). Evaluation of a distribution system in Ann Arbor, MI, revealed that all sample sites with residence times of fewer than 36 hours showed no symptoms of nitrification, whereas all sample sites with residence times greater than 72 hours showed symptoms (Skadsen 1993). Similarly, Wolfe et al. (1988) observed that increasing the mean HRT in a reservoir in Orange Country, CA, from 3.3 to 4.5 days spurred nitrification.

The presence of sediment and biofilms also favors nitrification. Sediment in a distribution system can result from incomplete removal of raw-water material, corrosion, or biological growth (Besner et al. 2002). Sediment and biofilms are most commonly found in low-flow sections of the pipe network and in storage tanks, where they can provide biocidal protection and possible nutrient availability. Although free chlorine is a considerably more active oxidant than monochloramine, sediment and biofilms will exert an oxidant demand on monochloramine, thereby limiting its ability to penetrate a biofilm. In fact, if the demand exerted by a biofilm is sufficiently large, monochloramine can be depleted in the outer portion of the biofilm. In this situation, the loss of biocide can be exacerbated by the potential for ammonia released during decomposition to migrate to the biofilm interior and fuel AOB activity (Harrington et al. 2003). For these reasons, more AOB have been found in sediment and biofilms than elsewhere in the distribution system (Wolfe et al. 1990).

Iron pipe in the distribution system has also been found to favor nitrification by promoting the growth of biofilms. As described in Section 2.1.2, reduced iron exerts a chloramine demand and therefore acts to inhibit microbial inactivation. In addition to promoting biofilm growth indirectly by exerting a biocide demand, it has been proposed that iron may support biofilm growth directly due to greater organic carbon adsorption by iron (Camper et al. 1996; Camper et al. 2003). Camper et al. (2003) found that a chlorine concentration of 0.2 mg/L was sufficient to control biofilm growth on PVC, cement, and epoxy, though not on ductile iron. The chlorine concentration remained constant in the presence of each substratum, indicating that the higher resistance of the iron-associated biofilm was not a result of higher chloramine demand. Instead, the authors proposed that the higher dissolved organic carbon (DOC) adsorption observed with iron contributes directly to biofilm growth by providing an energy source for heterotrophic bacteria. In another experiment yielding supporting conclusions, Camper et al. (1996) observed that, in the absence of a disinfectant, steel surfaces were consistently colonized by nearly 10-fold more bacteria than polycarbonate surfaces. Therefore, it was concluded that steel surfaces are capable of enhancing biofilm growth, rather than merely providing protection through disinfectant demand.

Nitrification occurrence is also highly dependent upon temperature. AOB and NOB growth rates are maximized at temperatures between 25 and 30°C (Harrington et al. 2003; Watson et al. 1981), and a decrease in temperature from 30 to 20°C has been found to slow growth by a factor of two to three (USEPA 1993). In addition to maximizing growth rates, high temperatures also favor nitrifying activity by significantly increasing the rate of chloramine decay (Section 2.1.2). Thus, there is a strong correlation between high temperatures and nitrification occurrence that is well documented (Lieu et al. 1993; Odell et al. 1996; Pintar et al. 2005; Wilczak et al. 1996; Wolfe et al. 1990). Nitrification is most prevalent at temperatures greater than 15 or 16°C (Wilczak et al. 1996; Wolfe et al. 1990), though it has been reported at temperatures as low as 6°C (Pintar et al. 2005). A study by Pintar and Slawson (2003) found that, once established, AOB could survive for extended periods at 6°C. Thus, while nitrification is most problematic during the summer months, it can occur at any time during the year.

System pH also influences nitrifying activity. Optimal conditions for growth are pH 7 to 8 for *Nitrosomonas* and 7.5 to 8 for *Nitrobacter* (Kirmeyer et al. 2004). Values of pH outside the range of 7 to 9 significantly reduce AOB activity (USEPA 1993). However, this relationship between pH and the growth of nitrifying bacteria is complicated by the fact that chloramine decay rates and chloramine disinfection efficacy are also influenced by pH. As described above, monochloramine is more stable at higher pH values. However, the ability of chloramines to inactive AOB decreases with increasing pH (Harrington et al. 2003). Thus, identifying the pH conditions that most favor nitrifying activity is challenging, and nitrification has been reported at pH values ranging from 6.5 to 10 (Odell et al. 1996).

2.2.2 Adverse Impacts on Water Quality

Nitrification can impact water quality in a number of ways. Perhaps most importantly, it can cause an accelerated loss of chloramine residual, likely due to the oxidant demand exerted by nitrite and/or the cometabolism of monochloramine by nitrifying bacteria (Section 2.1.2). This loss in chloramine residual can lead to violations of the SWTR requirement that a detectable residual be maintained throughout the distribution system. Even if the residual does not fall to zero, the system's disinfecting power will be compromised and bacterial regrowth may become an issue. This increased vulnerability to bacterial regrowth could lead to violations of the TCR. Nitrification also threatens water quality by increasing the nitrite and/or nitrate concentration. Nitrite (and nitrate, once it is converted to nitrite within the body) can interfere with the oxygen-carrying capacity of blood, and excess quantities can cause the potentially-fatal illness known as methemoglobinemia, or blue baby syndrome. For this reason, maximum contaminant levels (MCLs) for nitrite-N and nitrate-N are 1 mg/L and 10 mg/L, respectively. Though typical increases in nitrite-N are on the order of 0.05 to 0.5 mg/L, increases of greater than 1 mg/L are possible (Odell et al. 1996). Finally, nitrification can adversely impact water quality by reducing pH and alkalinity. Odell et al. (1996) report that 8.6 mg/L of bicarbonate is consumed during the complete oxidation of 1 mg/L of ammonia. The reductions in pH and alkalinity brought about by nitrification can increase a water's corrosivity and may result in violations of the Lead and Copper Rule (LCR).

2.2.3 Indicators of Occurrence

Episodes of nitrification are consistently associated with low chloramine concentrations. While it is still unclear whether chloramine residual is initially depleted because of nitrification or if nitrification occurs because chloramine residual is already low (Odell et al. 1996), the two are highly correlated. While a certain amount of chloramine decay is to be expected, excessive loss may be indicative of nitrifying activity. Skadsen (1993) reports that appreciable chloramine loss was detected in 61% of all distribution system sites sampled during an episode of nitrification. While typical chloramine loss was between 10 and 30%, the average loss during nitrification was 70%. Thus, excessive depletion of chloramine residual may be one of the best indicators of a nitrification episode.

A decrease in ammonia concentration and a corresponding increase in nitrite and/or nitrate concentration are also indicative of nitrification. As ammonia is consumed by AOB, the total ammonia (sum of ammonia-N and chloramine-N) concentration is depleted. In the absence of AOB activity, the total ammonia concentration should not change because chloramine decomposition transforms chloramine-N to ammonia-N, resulting in no net change in the total ammonia concentration. The free ammonia concentration is depleted only if the rate of ammonia oxidation by AOB is faster than the rate of ammonia release by chloramine decay. As the total (and possibly free) ammonia concentration decreases, the nitrite and/or nitrate concentration will increase. If NOB are not active and only partial nitrification occurs, the increase in nitrate concentration that may result from oxidation of nitrite by monochloramine may not be significant (see Section 2.1.2).

Increased heterotrophic plate counts (HPC) are commonly associated with nitrification episodes (McGuire et al. 2006; Skadsen 1993; Sullivan and McGuire 2005; Wilczak et al. 1996; Wolfe et al. 1990). The occurrence of high HPC during nitrification is likely due in large part to disinfectant loss associated with nitrification. Additionally, nitrifying bacteria release organic carbon in the form of biomass and soluble microbial products that can be used as a substrate for heterotrophic bacteria (Edwards et al. 2004). The levels of organic carbon secreted can be significant and can therefore contribute appreciably to HPC growth. Wolfe et al. (1990) found a strong correlation between HPC and AOB population, and proposed that HPC may be a good surrogate for direct AOB enumeration, which requires lengthy incubation periods. Thus, increases in HPC may mark increased nitrifying activity.

Decreases in pH, alkalinity, and dissolved oxygen (DO) concentration may also result from nitrification, though the utility of these parameters as indicators is marginal. As previously mentioned, nitrification acts to drive down pH and alkalinity. However, there are a number of complicating factors that can impact these parameters and therefore mask the changes that result from nitrification. Research has found that decreases in pH may (McGuire et al. 2006; Odell et al. 1996; Sullivan and McGuire 2005) or may not (Odell et al. 1996; Wilczak et al. 1996) correlate well with nitrification. Decreases in alkalinity have not typically been detected during nitrification (Odell et al. 1996; Wilczak et al. 1996). DO concentration is also impacted by nitrifying activity. Depending on whether nitrification is partial or complete, 3 to 4 mg/L of DO will be consumed by the oxidation of 1 mg/L of ammonia (Odell et al. 1996). Although decreases in DO concentration have been observed during nitrification (Odell et al. 1996; Wilczak et al. 1996), difficulty with accurate measurement in the field limits its utility as an indicator.

2.2.4 Prevention and Control Strategies

Excess ammonia in the distribution system is one of the principal causative factors of nitrification. Therefore, minimizing the introduction of free ammonia into the distribution system is widely recommended. A maximum point-of-entry (POE) free ammonia-N concentration target of 0.1 mg/L has been proposed (Kirmeyer et al. 2004). Limiting the free ammonia concentration at the POE can be achieved by targeting an appropriate Cl_2:NH_3-N weight ratio (mg Cl_2:mg NH_3-N) for chloramine formation (see Section 2.1.1). At a 5:1 Cl_2:NH_3-N weight ratio, almost all free ammonia is eliminated. At lower values, appreciable ammonia may be released into the distribution system, where it can fuel nitrifying activity. Although employing optimum or near-optimum Cl_2:NH_3-N ratios is not always effective at preventing nitrification (Harrington et al. 2003; Wilczak et al. 1996), the practice is commonly recommended (Odell et al. 1996; Wolfe et al. 1990).

Temporary conversion from chloramines to free chlorine, often referred to as breakpoint chlorination, has been found to control nitrification During the disinfectant switch, the ammonia feed is terminated and sufficient free chlorine is added to oxidize the remaining chloramines and bring the system beyond breakpoint to create a free chlorine residual (see Section 2.1.1). During the period of chlorination, generally one month annually, nitrification episodes are typically terminated due to the elimination of ammonia in the system and to the limited resistance of AOB to free chlorine relative to chloramines (Wolfe et al. 1990). Breakpoint chlorination is reported to be the most effective control measure for a nitrification episode already under way (Odell et al. 1996), and a recent survey found that 23% of chloraminating utilities employ the practice (Seidel 2005). However, breakpoint chlorination provides little long-term improvement, and is not an effective preventative measure. DiGiano et al. (2002) found evidence of nitrification in a distribution system in Raleigh, NC, within two months after the switch back to chloramines. In another study, AOB were found to return to their pre-chlorination levels just two weeks after the return to chloramines, suggesting a short-term inhibitory effect of free chlorine (Pintar and Slawson 2003). There are a number of drawbacks associated with breakpoint chlorination. Recent research by Ferguson (2005) demonstrates that the switch to free chlorine (and back again) results in a transitional front of low total chlorine residual due to the breakpoint reactions. If HRT is sufficiently long, this front can persist for weeks. Also, increased HPC (Skadsen 1993) and coliform-positive samples (Odell et al. 1996; Wilczak et al. 1996) have been associated with the switch to free chlorine. This finding is typically attributed to increased biofilm sloughing, as free chlorine is more reactive with capsular material and is therefore more likely to loosen and release biofilm material than monochloramine. Finally, breakpoint chlorination causes a temporary increase in the formation of THMs and HAAs. Despite these drawbacks, the ability to terminate a nitrification episode in progress makes temporary chlorination a common practice.

Maximizing the removal of NOM in the treatment plant may help to prevent nitrification. While nitrifying bacteria are autotrophic and therefore do not depend on organic material for growth, minimizing NOM reduces the oxidant demand of the water, thereby limiting chloramine decay and ammonia release. Also, biodegradable organic matter (BOM) enhances biofilm growth (Ollos et al. 2003), which has been found to favor nitrifying activity (see Section 2.2.1). Additionally, the greater the concentration of organics present in the water during chloramine formation, the greater the potential for organic chloramine formation (Odell et al. 1996). Due to the poor biocidal capacity of organic chloramines, NOM can therefore impact the biological stability of the water by limiting disinfection efficacy (see Section 2.1.1). For these reasons, it is believed that maximizing NOM removal may prevent or delay nitrification occurrence. Indeed, some studies have found that enhanced removal of NOM can significantly delay the onset of nitrification (Harrington et al. 2002; Harrington et al. 2003). Others, however, have suggested that it may not be an effective preventative measure (Wilczak et al. 2003). Despite these inconsistent findings, maximizing NOM removal may be an advisable practice for utilities employing breakpoint chlorination in order to minimize the formation of THMs and HAAs during the chlorination period.

Increasing the chloramine concentration at the POE has been proposed as a means of preventing nitrification. Theoretically, higher chloramine residual can improve biological stability by increasing the inactivation of nitrifying bacteria. In practice, however, the approach has not met with much success. Wilczak et al. (1996) found that POE residuals as high as 6 mg/L did not prevent evidence of nitrification and concluded that a high POE chloramine concentration may not be a sufficient factor in nitrification prevention. In a study by Cunliffe (1991), AOB were found in 21% of samples with greater than 5 mg/L of chloramines, also indicating that high residuals may not be effective at preventing nitrification. Increasing the POE residual also appears to be an ineffective control strategy, as a dose of 8 mg/L was found to be unsuccessful at terminating a nitrification episode already in progress (Skadsen 1993). Increasing the chloramine residual may, in fact, exacerbate nitrification by contributing more ammonia nitrogen to the system. A model developed by Woolschlager et al. (2001a) found that nitrification cannot be effectively controlled by an increase in residual because ammonia release caused by chloramine decomposition can fuel AOB growth faster than chloramine can inactivate the bacteria. Also, high chloramine residual has been found to increase the rate of chloramine autodecomposition, as described in Section 2.1.2. Additionally, increasing chloramine residual may result in T&O problems and increased formation of chloramine-related byproducts, such as CNCl and NDMA. Research by Choi and Valentine (2002) found that NDMA formation was positively correlated with high chloramine residual.

Increasing finished-water pH may help to prevent nitrification. Raising the pH to a level outside the range of conditions favored by nitrifying bacteria (pH 7 to 9) can restrict nitrifying activity. The reduced rate of chloramine decay at increasing pH values can contribute to the success of this strategy. However, the reduced chloramine disinfection efficacy associated with increased pH values acts to offset these benefits. Whether the advantages associated with raising the pH are sufficient to offset the disadvantages is dependent upon numerous factors specific to each system. Skadsen (2002) reports that increasing the finished-water pH at the Ann Arbor (MI) Water Treatment Plant to 9.3 had a significant impact on nitrification occurrence. Prior to the change in pH, nitrification occurred every summer, and increasing the pH prevented nitrification in seven of the next eight years. Song et al. (1999) found that raising the pH to 9 prevented nitrification in one system but not in another. As with many of the other prevention and control strategies, increasing the pH has implications that reach beyond nitrification. Increased pH offers the added benefits of fewer T&O problems due to increasingly unfavorable conditions for dichloramine formation, as well as reduced corrosion potential. However, increased pH also may result in significant calcium carbonate deposition (Skadsen 2002).

Two additional prevention and control measures are periodic flushing/pigging of the pipe network and minimizing HRT to the extent feasible. Flushing/pigging pipelines can remove biofilms, as well as sediment and tubercles that can harbor nitrifying bacteria. Flushing also removes nitrified water. Odell et al. (1996) report that regular high-velocity flushing and pigging may be effective at both prevention and control of nitrification. Skadsen (1993) reports that the discontinuation of a flushing program likely contributed to nitrification occurrence. As previously described, HRT can contribute to nitrification by allowing time for nitrifying bacteria to grow and for chloramine decomposition reactions to take place. Therefore, minimizing HRT may be a good long-term improvement strategy (Odell et al. 1996). This can be accomplished by increasing reservoir drawdown and tank turnover, retrofitting tanks to prevent short-circuiting, looping dead-end mains, and implementing a regular flushing program.

A relatively new technology being evaluated for use in nitrification prevention and control is the introduction of chlorite ion (ClO_2^-) into the distribution system. It has been proposed that the oxidation of ammonia by AOB may take place within AOB cell walls, causing an increasingly acidic environment within the cell due to hydrogen release by the oxidation reaction. Chlorite ion can diffuse into the cell, react in the acidic environment to form chlorine dioxide (ClO_2), and inactivate the AOB (McGuire et al. 1999). Chlorite ion, which can be introduced into the distribution system as a byproduct of primary disinfection with chlorine dioxide or as a point-of-entry additive in the form of sodium chlorite ($NaClO_2$), has performed well in pilot-scale studies (McGuire et al. 2006; Sullivan and McGuire 2005). One study found that a continuous ClO_2^- feed of 0.2 mg/L was sufficient to prevent nitrification, and intermittent slug feeds of 0.2 mg/L for seven days were able to stop nitrification, although the time to the onset of nitrification was reduced after each treatment (Sullivan and McGuire 2005). Another pilot-scale study found that a 0.1 mg/L continuous feed of ClO_2^- was sufficient to control nitrification, and a week-long slug feed of 0.2 mg/L was able to halt serious nitrification episodes in progress, although nitrification episodes subsequently resumed and required higher doses to completely control (McGuire et al. 2006). These results suggest that the addition of ClO_2^- may be a highly effective preventative measure, though perhaps not an appropriate control measure. Research by Hy~~ay~~nes and Knowles (1983) corroborates findings that nitrifying activity may be inhibited by ClO_2^-. There are, however, concerns about adding ClO_2^- to drinking water systems as it is a regulated contaminant. The current maximum contaminant level goal (MCLG) is 0.8 mg/L, and the MCL is 1 mg/L.

2.3 N-NITROSODIMETHYLAMINE

A compound that has been of increasing concern in treated drinking water is NDMA. Research has shown nitroso compounds to be carcinogenic (Charrois and Hrudey, 2007). NDMA is primarily found in chloraminated systems because of the presence of ammonia and monochloramine. Charrios and Hrudey (2007) found NDMA in higher concentrations and frequency in chloraminated distribution systems than in distribution systems using free chlorine. The maximum formation occurs at sub-breakpoint levels, suggesting that NDMA formation may be dependent on the disinfectant concentration and residence time (Charrois and Hrudey, 2007).

Various pathways have been proposed for the formation of NDMA in drinking water systems. The interaction between monochloramine and organic nitrogen species results in NDMA formation in full-scale water and wastewater treatment plants. Mitch and Sedlak (2002) found that the formation of NDMA occurred via the intermediate unsymmetrical dimethylhydrazine (UDMH). The initial reaction is a two-electron substitution reaction between ammonia and monochloramine in the presence of excess hydrogen ions (Mitch and Sedlak, 2002). The intermediate is then oxidized to form UDMH and hydrochloric acid. The reaction is shown in Equation 2.12.

$$\underset{\text{organic nitrogen}}{NH_2Cl + (CH_3)_2NH_2^+} \xleftrightarrow{H+} NH_2Cl + (CH_3)_2NH \rightarrow \underset{\text{UDMH}}{(CH_3)_2NH_2} + HCl \qquad (2.12)$$

The UDMH is converted to NDMA through the formation of dimethyldiazene (DMD). This intermediate is formed through the oxidation of UDMH in the presence of monochloramine (Mitch and Sedlak, 2002).

$$\underset{\text{UDMH}}{(CH_3)_2NNH_2} \xrightarrow{NH_2Cl} \underset{\text{DMD}}{(CH_3)_2NN} \qquad (2.13)$$

DMD may form different products under different conditions. The most common product in drinking water systems is NDMA because of the excess monochloramine. DMD is oxidized by monochloramine to produce NDMA, ammonium, and chloride. The final NDMA reaction is

$$\underset{\text{DMD}}{(CH_3)_2NN} + NH_2Cl \xrightarrow{H_2O} NH_4^+ + Cl^- + \underset{\text{NDMA}}{(CH_3)_2NNO} \qquad (2.14)$$

Once formed, NDMA is persistent in water distribution systems. Increased ammonia concentrations from the breakdown of chloramines have led to increasing concerns about NDMA formation.

While NDMA is listed by the EPA as a probable human carcinogen (USEPA, 2002), it is not yet regulated because of a lack of knowledge of its occurrence in finished drinking water. Several states and Canadian provinces have established maximum contaminate levels (MCLs) for NDMA. The State of California adopted a Notification Level of 0.01 μg/L, or 10 ng/L, and the province of Ontario has a MCL of 9 ng/L (Charrois and Hrudey, 2007). With continued research on the formation and occurrence of NDMA, regulation of NDMA is expected to occur at a broader level in the future.

CHAPTER 3 – METHODS

3.1 GENERAL APPROACH

Five chloraminating drinking water utilities in North Carolina were studied to determine the degree to which each distribution system experienced symptoms of nitrification in recent years, as well as to evaluate treatment plant operating practices and finished-water quality characteristics that may influence nitrification potential. The project participants were those members of the North Carolina Urban Water Consortium using combined chlorine for secondary disinfection, namely the Durham Environmental Resources Department, Fayetteville Public Works Commission, Greenville Utilities Commission, Orange Water and Sewer Authority (OWASA), and Raleigh Public Utilities Department. The locations of these utilities are shown in Figure 3.1, and a summary of utility characteristics is provided in Table 3.1.

The data analyzed during this study were provided by the participating utilities. Each utility provided historical data for a period of up to four years, depending on when it began to employ chloramines. These data were then analyzed to assess, to the extent possible, each system's nitrification potential and the operating practices that directly influence that potential, as well as the extent of nitrification occurrence.

Limited sampling for NDMA was also conducted in the Durham and Raleigh distribution systems. Selected sampling locations for NDMA analysis were those with low chloramine residuals.

Figure 3.1: Locations of participating utilities

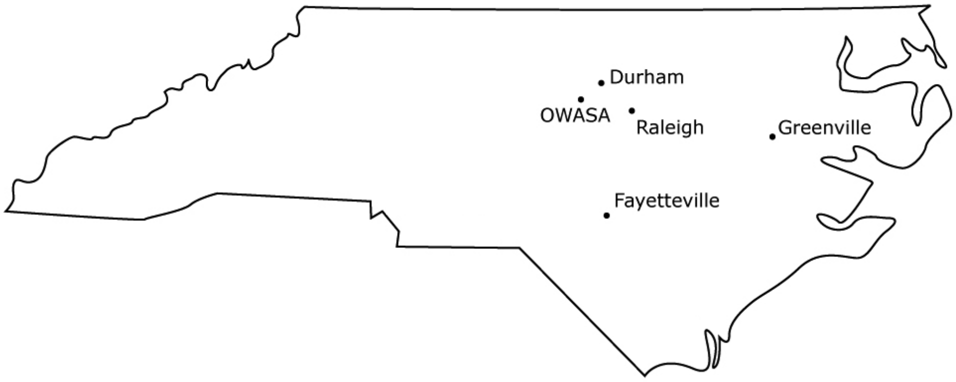


Table 3.1: Summary of utility characteristics

	UTILITY				
	Durham	Fayetteville	Greenville	OWASA	Raleigh
Total System Capacity (MGD)	61 [1]	50 [3]	22.5 [4]	20 [6]	86 [8]
Average Daily Demand (MGD)	32 [1]	22 [3]	10 [4]	9 [6]	47 [9]
Population Served	183,000 [2]	177,000 [3]	76,000 [5]	75,000 [7]	344,000 [5]
Miles of DS Piping	1,100 [2]	1,173 [3]	565 [4]	337 [6]	1616 [8]
Number of Treatment Plants	2	2	1	1	1 [10]
Chloramination Start Date	1/29/2002	3/1/2003	12/10/2003	2/1/2002	8/21/1993

[1] Durham Environmental Resources Department (2006); [2] Ferguson (2005); [3] Fayetteville Public Works Commission (2006); [4] Greenville Utilities Commission (2006); [5] Han (2005); [6] Orange Water and Sewer Authority (2006); [7] Monschein (2006); [8] CDM (2006); [9] Raleigh Public Utilities Department (2006); [10] Data collected were from the E.M. Johnson WTP only; the G.G. Hill WTP (2.2 MGD capacity) was not included in this analysis

3.2 INFORMATION COLLECTED

Various water quality data were collected from each utility's water treatment plant(s) (WTP), and from sampling sites located throughout each distribution system (DS). The data requested from the treatment plants included the point-of-entry (POE) concentrations of free and combined chlorine, free and total ammonia, nitrite, nitrate, total organic carbon (TOC), and dissolved oxygen (DO). The POE water temperature values (assumed to be equal to the raw water temperatures) and pH were also requested. The utilities were also asked to provide the data necessary to calculate the Cl_2:NH_3-N ratios used to form chloramines. These data comprised the free chlorine residuals immediately prior to ammonia addition, the ammonia dosages, and the doses of any additional free chlorine added at the point of ammonia addition. Daily average values were requested for each of these treatment plant parameters.

The data requested for the distribution system sampling locations included concentrations of free and combined chlorine, free and total ammonia, nitrite, nitrate, and dissolved oxygen. HPC and pH data were also requested, as well as the approximate water ages at the various sampling locations.

3.3 ANALYSES PERFORMED

To the extent made possible by the system data provided, the analyses described below were performed on each utility's treatment plant(s) and distribution system. (Periods during which utilities made a temporary switch from chloramines to free chlorine were excluded from all analyses.) The results of these analyses were compared to standard industry-wide practices and recommendations.

3.3.1 Water Treatment Plant

The overall magnitude and consistency of each utility's POE total or combined chlorine concentrations were evaluated, as were the pH and TOC concentrations at the POE. The data were also examined to determine the length and consistency of temporary conversions to free chlorine. The free ammonia concentrations at the POE were also analyzed. Where POE total ammonia concentrations were provided in lieu of free ammonia concentrations, the values of free ammonia were calculated by first converting the combined chlorine concentration from mg/L as Cl_2 to mg/L as N (Equation *3.1*), then subtracting this value from the total ammonia value (Equation *3.2*). Where combined chlorine concentrations were not provided directly, 100% of the total chlorine concentration was assumed to be combined chlorine.

$$\text{Chloramine-N (mg/L as N)} = \frac{\text{Combined Chlorine (mg/L as Cl}_2\text{)}}{5\ \text{(mg as Cl}_2\text{)/(mg as N)}} \qquad (3.1)$$

$$\text{Free Ammonia (mg/L as N)} = \text{Total Ammonia-N} - \text{Chloramine-N} \qquad (3.2)$$

The Cl_2:NH_3-N weight ratios used to form monochloramine were also analyzed. These ratios were calculated by first determining the total concentration of free chlorine available at the point of ammonia addition (PAA), then dividing this value by the concentration of ammonia dosed at the PAA (Equations *3.3* and *3.4*). It should be noted that implicit to Equation *3.4* is the assumption that any raw-water ammonia is oxidized during pretreatment, and thus does not contribute to the concentration of ammonia available for chloramine formation. Given that free chlorine (and in some cases ozone) is used for oxidation and primary disinfection at each of the participating utilities, oxidation of any raw-water ammonia is expected.

$$\text{Total Cl}_2\text{ at PAA (mg/L as Cl}_2\text{)} = \text{Residual Cl}_2\text{ at PAA} + \text{Cl}_2\text{ Dosed at PAA} \qquad (3.3)$$

$$\text{Cl}_2\text{:NH}_3\text{-N Weight Ratio (mg Cl}_2\text{/mg N)} = \frac{\text{Total Cl}_2\text{ at PAA (mg/L as Cl}_2\text{)}}{\text{NH}_3\text{ Dosed at PAA (mg/L as N)}} \qquad (3.4)$$

Where monochloramine was formed using Cl_2:NH_3-N weight ratios less than the 5:1 theoretically optimum value discussed in Section 2.1.1, the predicted values of excess free ammonia were calculated and compared to the values measured at the POE. The predicted values of excess ammonia were calculated by first determining the concentration of ammonia consumed by monochloramine formation (Equation *3.5*), then subtracting this value from the concentration of ammonia dosed at the PAA (Equation *3.6*).

$$\text{NH}_3\text{ for NH}_2\text{Cl (mg/L as N)} = \frac{\text{Total Cl}_2\text{ at PAA (mg/L as Cl}_2\text{)}}{5\ \text{(mg/L Cl}_2\text{ as Cl}_2\text{)/(mg/L NH}_3\text{ as N)}} \qquad (3.5)$$

$$\text{Predicted Excess NH}_3\text{ (mg/L as N)} = \text{NH}_3\text{ Dosed at PAA} - \text{NH}_3\text{ for NH}_2\text{Cl} \qquad (3.6)$$

Conversely, where monochloramine was formed using Cl_2:NH_3-N weight ratios greater than 5:1, the predicted values of total chlorine residual were calculated and compared to the values measured at the POE. The predicted total chlorine residual values were calculated by first determining the concentration of free chlorine in excess of that consumed by monochloramine formation (Equations *3.7* and *3.8*). (It should be noted that the concentration of free chlorine consumed by monochloramine formation calculated using Equation *3.8* is equal to the concentration of monochloramine formed, as indicated by the stoichiometry of Reaction *2.1*.) The predicted total chlorine residuals were then calculated as shown by Equation *3.9*, which is based upon the assumption that excess free chlorine reacts to destroy monochloramine through breakpoint reactions (see Section 2.1.1) at a 1:1 ratio of free chlorine to monochloramine. In other words, a breakpoint Cl_2:NH_3-N weight ratio of 10:1 was assumed. If the Cl_2:NH_3-N ratio is sufficiently high, Equation *3.9* may yield a negative number, implying that the breakpoint has been exceeded. In this case, all residual chlorine exists as free chlorine, and the value of free chlorine is the absolute value of the concentration calculated using Equation *3.9*.

$$\mathrm{Cl_2\ for\ NH_2Cl\ (mg/L\ as\ Cl_2)} = \frac{5\ \mathrm{(mg/L\ Cl_2\ as\ Cl_2)}}{\mathrm{(mg/L\ NH_3\ as\ N)}} \times \mathrm{NH_3\ Dosed\ at\ PAA\ (mg/L\ as\ N)} \qquad (3.7)$$

$$\mathrm{Excess\ Cl_2\ (mg/L\ as\ Cl_2)} = \mathrm{Total\ Cl_2\ at\ PAA} - \mathrm{Cl_2\ for\ NH_2Cl} \qquad (3.8)$$

$$\mathrm{Predicted\ Total\ Cl_2\ (mg/L\ as\ Cl_2)} = \mathrm{Cl_2\ for\ NH_2Cl} - \mathrm{Excess\ Cl_2} \qquad (3.9)$$

3.3.2 Distribution System

Where distribution system data were limited to only those sites identified by a utility as particularly vulnerable to nitrification, each site was analyzed to the full extent permitted by the data set. However, where data were provided for all sampling locations within the distribution system, the sites were sorted by total chlorine concentration prior to analysis. An analytical survey by Wilczak et al. (1996) found that over 90% of nitrification symptoms occurred at chloramine concentrations less than 2 mg/L. Therefore, only those sites with one or more detections of total chlorine concentration below 2 mg/L (during chloraminating months only) were evaluated.

In addition to the identification of low disinfectant residuals, the distribution system data were analyzed (to the extent that necessary data were available) for several other symptoms of nitrification. These symptoms included increases in nitrite and/or nitrate concentration and decreases in free and/or total ammonia concentration, as well as decreases in pH and dissolved oxygen concentration. Given that the water age at each distribution system location is highly variable and largely unknown, distribution system parameters could not be compared to POE values for that same parameter on any particular day. Instead, the distribution system data were compared to average POE values. Where POE values were stable, averages were taken across the full period of analysis. Where POE values were less consistent, monthly average values were used for comparison. Lastly, the relationship between the symptoms of nitrification listed above and HPC and approximate water age was also explored.

3.4. N-NITROSODIMETHYLAMINE

Samples were taken at selected sites in the Durham and Raleigh distribution systems. The sites were chosen based on previously observed low total chlorine residuals and elevated concentrations of nitrite and/or nitrate. The site in central downtown Durham was Site E30, City Hall. The sites in the Raleigh system were in the town of Wendell, a suburb using Raleigh water.

In collecting the samples, the water was allowed to run for five minutes before samples were taken. The samples were analyzed for total chlorine residual using a Hach Pocket Colorimeter.

For NDMA analysis, the samples were collected in two 500 mL amber glass bottles with Teflon lids. The samples were immediately treated with a trace amount of ascorbic acid (~0.1 mg) to quench the residual monochloramine, and placed in a cooler with blue ice packs for transport back to the UNC laboratories where it was stored at 4°C. Within 48 hours after collection, the samples were spiked with 20 ng/L d_6-NDMA (Sigma-Aldrich) as an internal reference standard and shipped to the University of Waterloo in Ontario, Canada for NMDA analysis. The cooler contained frozen blue ice packs to prevent NDMA degradation.

The samples were analyzed using gas chromatography/mass spectrometry (GC/MS) following the procedure of Moffat (2006) in *Nitrosamines Sampling and Analytical Methods.* The samples were analyzed only for NDMA. Ambersorb XEN-572 was used to extract NDMA from the water. The Ambersorb XEN-572 was conditioned by heating the resin at 320°C for at least three hours. To a 500 mL d_6-NDMA-spiked sample, 400 µL of Ambersorb XEN-572 was added. The bottle was shaken at 250 rpm for 60 minutes. The solution was filtered using a Whatman #4 filter with a pore size of 20-25 µm under vacuum into a vacuum flask. The bottle was rinsed with high purity water to ensure the complete transfer of Ambersorb XEN-572 resin onto the filter paper. The filter was kept under vacuum to remove most of the water from the resin. The filter paper was then transferred to an aluminum dish and dried for 30-60 minutes in a fume hood. The dried resin was then placed in a 400 µL autosampler vial insert. To the vial, 350 µL of dichloromethane was slowly added using a 1 mL syringe to prevent "bumping" of the beads that could result in loss of the extract. The 400 µL vials were placed in 2 mL autosampler vials and capped. The samples were analyzed immediately using GC/MS. All samples were analyzed in duplicate to verify the reproducibility of the procedure.

CHAPTER 4 – RESULTS

The analyses described in Section 3.3 were performed to the extent made possible by the dataset provided by each utility, and the results of these analyses are discussed in the following sections. (It should be noted that none of the analyses described below were performed on data provided for months during which the utilities practiced free chlorination.) The limited set of NDMA results are also presented.

4.1 DURHAM

A summary of the treatment plant and distribution system data provided by Durham is shown in Table 4.1.

Table 4.1: Summary of system data provided (Durham)

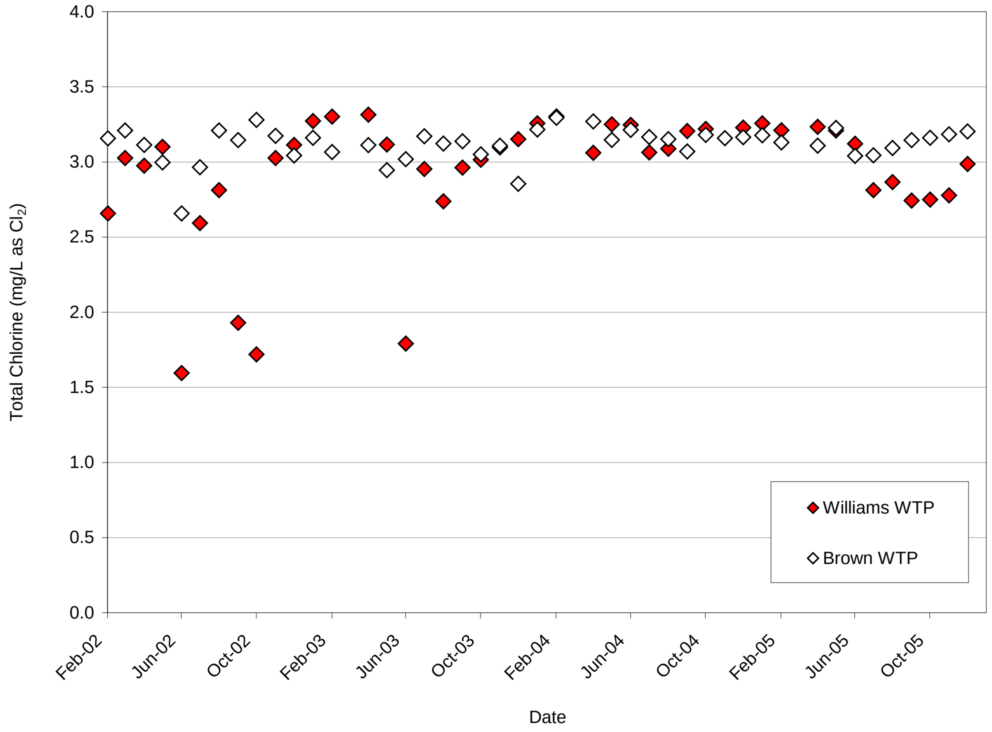
SYSTEM LOCATION	PERIOD	INFORMATION PROVIDED	
Point of NH_3 Addition (PAA)	2/02 - 12/05	Free Cl_2 (Before NH_3)	✓
		Add'l Cl_2 Dosed (w/ NH_3)	-
		NH_3 Dosed	✓
Point of Entry (POE)	2/02 - 12/05	Daily Temp. (Raw Water)	✓
		Min. Daily Total Cl_2	✓[1]
		Daily pH	✓
		Daily Free NH_3	✓
		NO_2^-	-
		Weekly NO_3^-	✓
		Weekly DO	✓
		Monthly TOC	✓[2]
Distribution System (DS)	1/03 - 6/05	Total Cl_2	✓
		pH	-
		NH_3	-
		NO_2^-	-
		NO_3^-	✓
		HPC	✓
		DO	-
		Approximate Water Age	-

[1] Minimum daily POE Cl_2 residuals provided (average daily values not available);

[2] Parameter available from April 2003 through July 2005

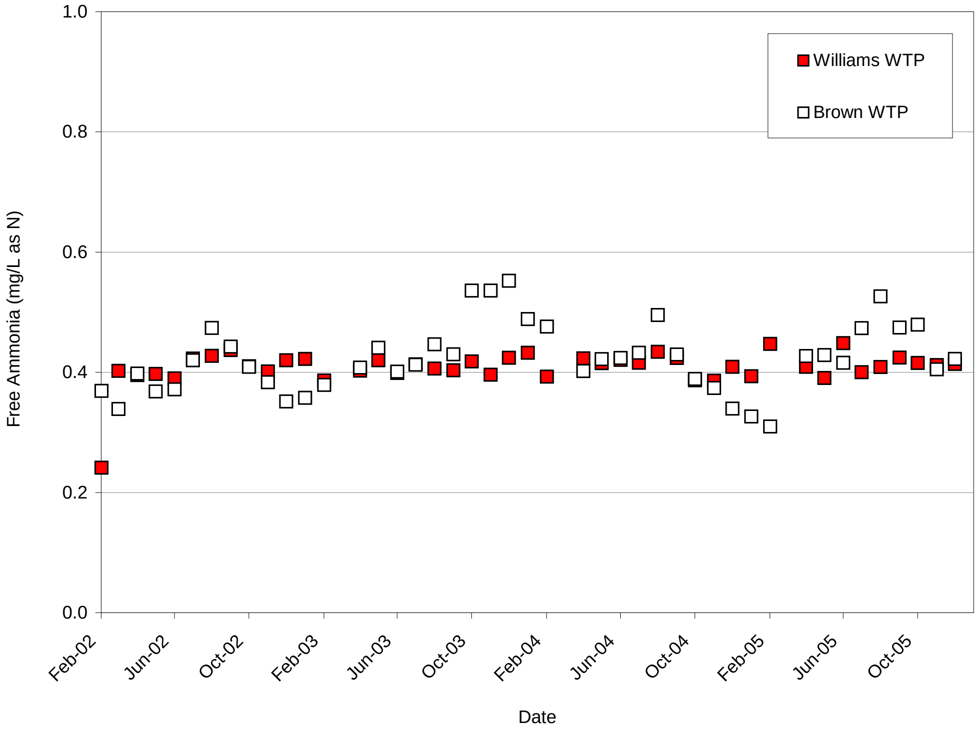
The monthly average total chlorine concentrations at the POE to the distribution system from the Brown WTP and the Williams WTP are shown in Figure 4.1. With the exception of four months of low POE residuals at the Williams WTP in 2002 and 2003, there was reasonable consistency between the two plants. The monthly average total chlorine residuals generally fluctuated between 2.6 and 3.3 mg/L (excluding the four months of low residuals at the Williams WTP), and the two-plant average over the 4-year period was 3.0 mg/L.

Figure 4.1: Monthly average total chlorine concentrations at the point of entry to the distribution system from the Brown and Williams Water Treatment Plants (Durham)



The Cl_2:NH_3-N ratios used to form monochloramine could not be calculated for either treatment plant due to lack of free chlorine dosage data at the PAA that were necessary to determine the total concentration of free chlorine present at the PAA (see Equation *3.3*), as indicated in Table 4.1. However, the excess free ammonia measured at each POE suggests that the Cl_2:NH_3-N weight ratios used at each plant may have been significantly below the 5:1 theoretically optimum ratio. The excess free ammonia concentrations at each treatment plant are shown in Figure 4.2. The monthly average free ammonia concentrations at the Brown WTP ranged from 0.24 to 0.45 mg/L, and the values at the Williams WTP fluctuated between 0.31 and 0.55 mg/L. The 4-year average free ammonia concentrations at the Brown and Williams WTPs were 0.42 mg/L and 0.41 mg/L, respectively. These data suggest that increasing the Cl_2:NH_3-N ratio (or decreasing the ammonia dose) relative to current operations may be advisable in order to minimize the release of free ammonia into the distribution system.

Figure 4.2: Monthly average free ammonia concentrations at the point of entry to the distribution system from the Brown and Williams Water Treatment Plants (Durham)



Although the Cl_2:NH_3-N ratios used to form monochloramine could not be calculated using Equation *3.3* because of the unknown free chlorine dosages at the PAA, sufficient data were available to approximate the ratios used. The appreciable concentrations of excess free ammonia present at the POE from each treatment plant suggest that free chlorine was the limiting reactant in the formation of monochloramine, and thus suggest that all free chlorine present at the PAA was converted to combined chlorine. Therefore, the total concentration of free chlorine present at the PAA can be assumed to be equal to the concentration of total chlorine at the POE. These chlorine concentrations can then be divided by the ammonia dosages at the PAA to approximate the Cl_2:NH_3-N weight ratios (see Equation *3.4*). These approximated ratios are shown in Figure 4.3. The monthly average approximated Cl_2:NH_3-N ratios used at the Brown WTP ranged from 3.0:1 to 4.0:1. Excluding the four low ratios corresponding to atypically low total chlorine residuals at the POE from the Williams WTP in 2002 and 2003, the monthly average approximated Cl_2:NH_3-N ratios used at the Williams WTP ranged from 2.7:1 to 4.4:1. The 4-year average ratios at the Brown and Williams WTPs were 3.4:1 and 3.1:1, respectively. (It should be noted that the ammonia dosages used to calculate these ratios were approximated by the utility using pounds of ammonia dosed and the daily raw water volume in lieu of the actual volume of water to which ammonia was added. Thus, the true ammonia dosages should be higher than those reported by the utility, and the true Cl_2:NH_3-N ratios should be somewhat lower than those shown in Figure 4.3.)

The theoretical (predicted) values of excess free ammonia present at the POE can also be approximated (using Equations *3.5* and *3.6*) by assuming the total concentration of free chlorine at the PAA to be equal to the concentration of total chlorine at the POE. The approximated theoretical free ammonia concentrations are shown in Figure 4.4, along with the free ammonia concentrations measured at the POE. The two-plant monthly average predicted values range from 0.18 to 0.48 mg/L and average 0.36 mg/L over the 4-year period of analysis, and the two-plant monthly average measured values ranged from 0.31 to 0.49 mg/L and averaged 0.41 mg/L over the 4-year period. The reasonable consistency between these predicted and measured concentrations of excess free ammonia validates the assumption that the total concentration of free chlorine available at the PAA was approximately equal to the total chlorine concentration at the POE.

The average pH values at the POE to the distribution system from the Brown WTP and Williams WTP over the 4-year period of analysis were 8.1 and 8.2, respectively, with a standard deviation at each plant of 0.3. The average TOC concentrations at the POE from the Brown and Williams WTPs over the 2.5-year period for which TOC data were provided were 2.4 mg/L and 3.0 mg/L, respectively, with standard deviations of 0.3 mg/L and 0.6 mg/L. A one-month switch to free chlorine was made in March of each year following the year in which chloramination began.

Figure 4.3: Approximated monthly average chlorine-to-ammonia ratios at the Brown and Williams Water Treatment Plants (Durham)

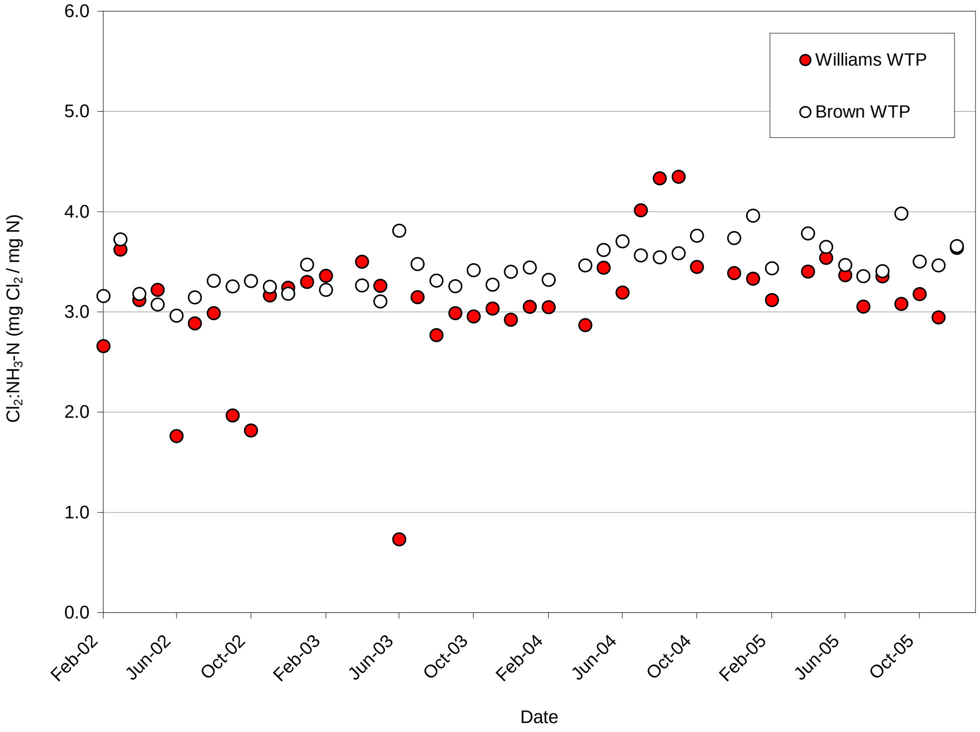
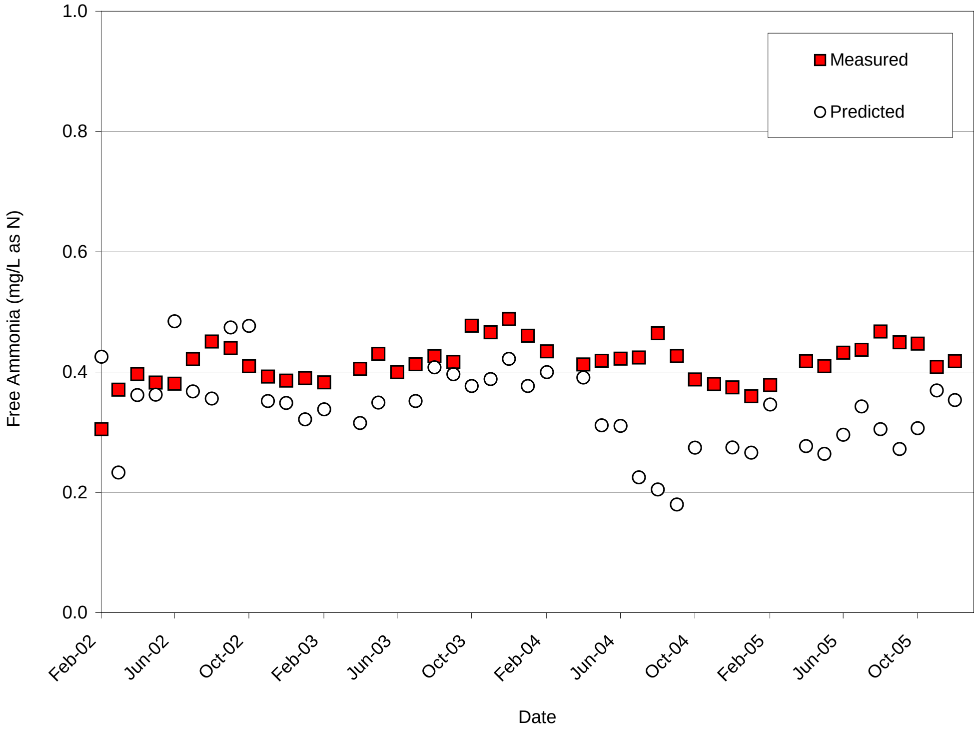


Figure 4.4: The two-plant monthly average predicted and the two-plant monthly average measured free ammonia concentrations at the point of entry to the distribution system (Durham)



Water quality data were provided for the 32 distribution system sampling sites considered most vulnerable to nitrification by the utility. While total chlorine concentrations occasionally reached values below 1.5 mg/L at several of these sites, an overwhelming majority of samples had total chlorine residuals above 2.0 mg/L. Two notable exceptions were sites E30 and E40, located in downtown Durham, each of which experienced prolonged periods of low disinfectant residual. The total chlorine concentrations measured in all samples taken from sites E30 and E40 over the period of analysis are shown in Figures 4.5 and 4.6, respectively, along with the two-plant average total chlorine concentration at the POE. (The total chlorine residuals at the POE from the Brown and Williams WTPs were averaged over the 2.5-year period for which distribution system data were provided.) The chlorine residual at site E30 reached a low of 0.40 mg/L in October 2004, and site E40 experienced several residual concentrations below 1.5 mg/L.

Figure 4.5: Total chlorine concentrations at distribution system site E30 and the two-plant average total chlorine concentration at the point of entry to the distribution system (Durham)

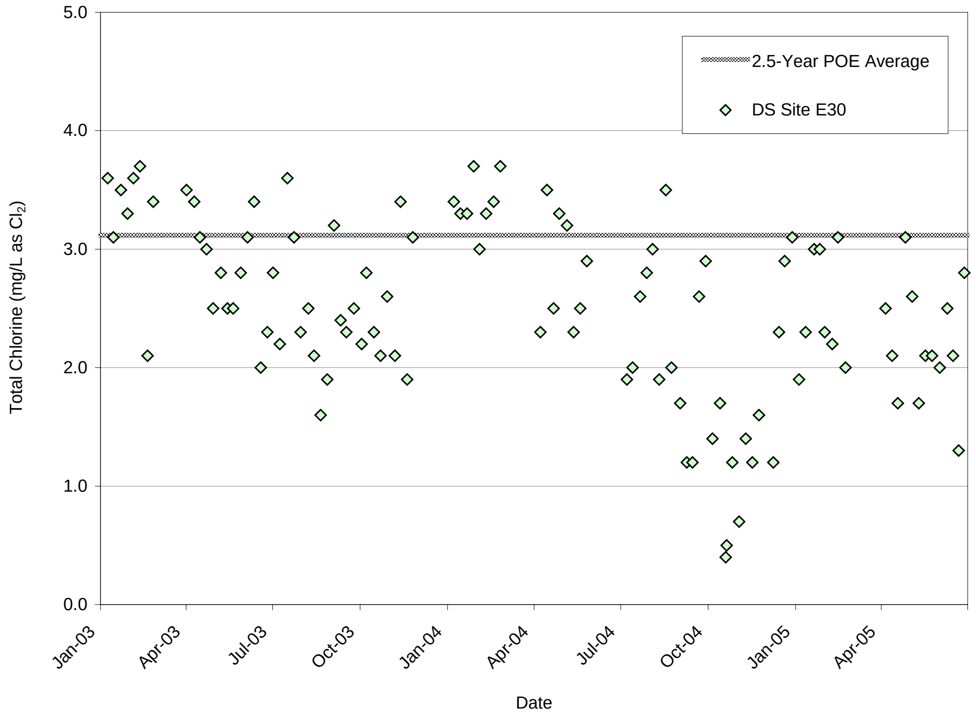
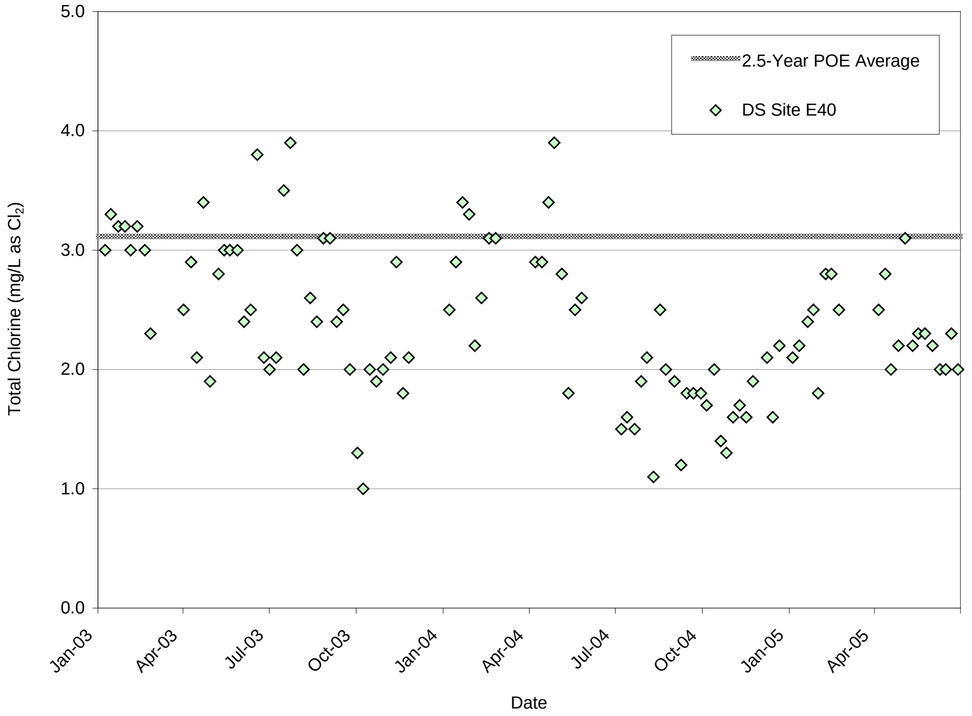


Figure 4.6: Total chlorine concentrations at distribution system site E40 and the two-plant average total chlorine concentration at the point of entry to the distribution system (Durham)



Data were evaluated for increases in nitrate concentration between the POE and each distribution system location. (Nitrite data were not routinely collected at the treatment plant or in the distribution system, thus nitrite concentration could not be assessed for change.) While stable nitrate concentrations do not necessarily indicate an absence of nitrifying activity, as partial nitrification directly impacts only nitrite concentration, an increase in nitrate concentration does indicate the presence of nitrifying activity. Nitrate concentrations in Durham's distribution system were generally consistent with POE values at all locations except site E30. At this location, significant increases in nitrate concentration were detected during a period of prolonged low disinfectant residual in October and November 2004, as shown in Figure 4.7. This finding is suggestive of nitrification, and HPC data collected at this location (shown in Figure 4.8) offer further support of nitrification occurrence. HPC values were highest during the period of low disinfectant residual and increased nitrate concentration. Additionally, the raw water temperature at the onset of the increased nitrate concentration and the significant loss of disinfectant residual was approximately 24°C – a temperature quite favorable for nitrifying activity. As shown in Table 4.1, the necessary data were not available to determine whether or not decreases in free and/or total ammonia concentration, pH, or DO concentration also occurred at this location during this period.

Figure 4.7: Total chlorine concentrations at distribution site E30 and the change in nitrate concentrations between the point of entry to the distribution system and site E30 (Durham)

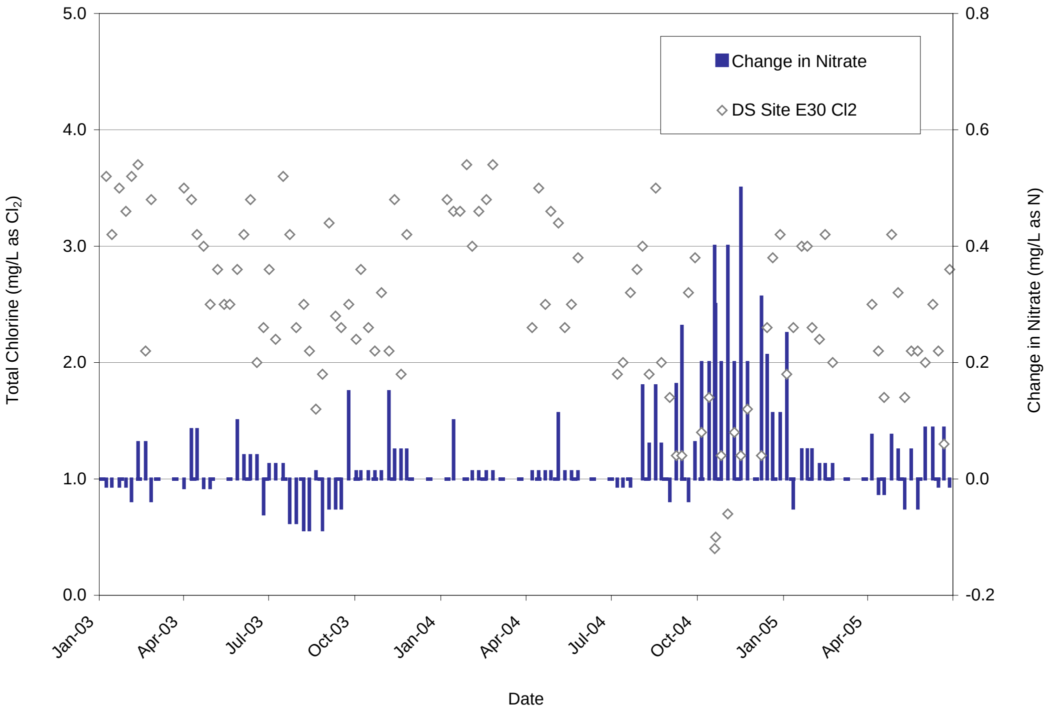
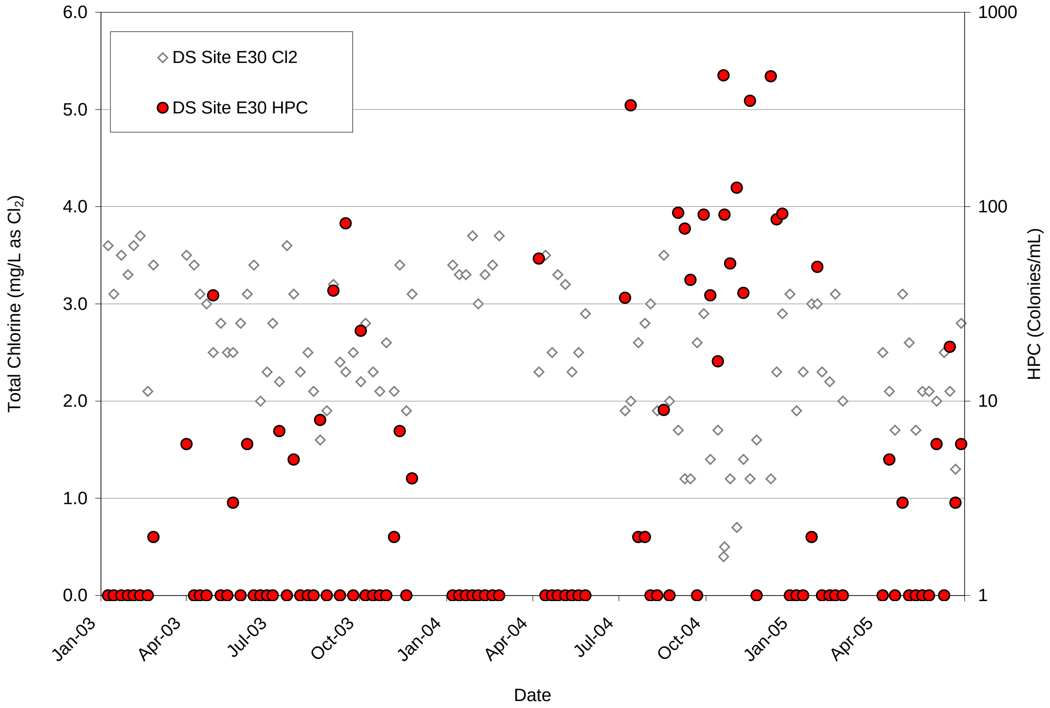


Figure 4.8: Total chlorine concentrations at distribution site E30 and HPC values at site E30 (Durham)



4.2 FAYETTEVILLE

A summary of the system data provided by Fayetteville is shown in Table 4.2.

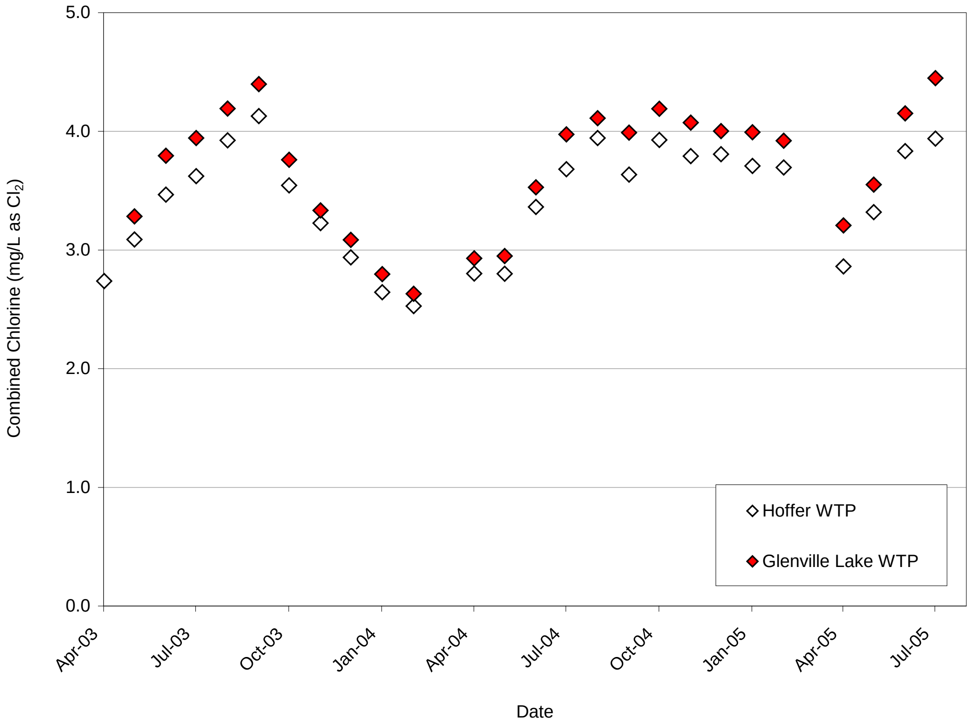
Table 4.2: Summary of system data provided (Fayetteville)

SYSTEM LOCATION	PERIOD	INFORMATION PROVIDED	
Point of NH_3 Addition (PAA)	5/03 - 7/05	Free Cl_2 (Before NH_3)	✓[1]
		Add'l Cl_2 Dosed (w/ NH_3)	✓
		NH_3 Dosed	✓
Point of Entry (POE)	3/03 - 7/05	Daily Temp. (Raw Water)	✓
		Min. Daily Combined Cl_2	✓[2]
		Daily pH	✓
		Daily Free NH_3	✓
		NO_2^-	–[3]
		NO_3^-	–[3]
		DO	–
		Monthly TOC	✓
Distribution System (DS)	11/03 - 7/05	Combined Cl_2	✓
		pH	-
		NH_3	-
		NO_2^-	–[3]
		NO_3^-	–[3]
		HPC	✓[4]
		DO	-
		Approximate Water Age	✓

[1] Data provided for Glenville Lake WTP only; [2] Minimum daily POE Cl_2 residuals provided (average daily values not available); [3] Data provided not used due to analytical uncertainty (e.g. reported nitrite levels on the order of 3.0 mg/L); [4] Limited data provided

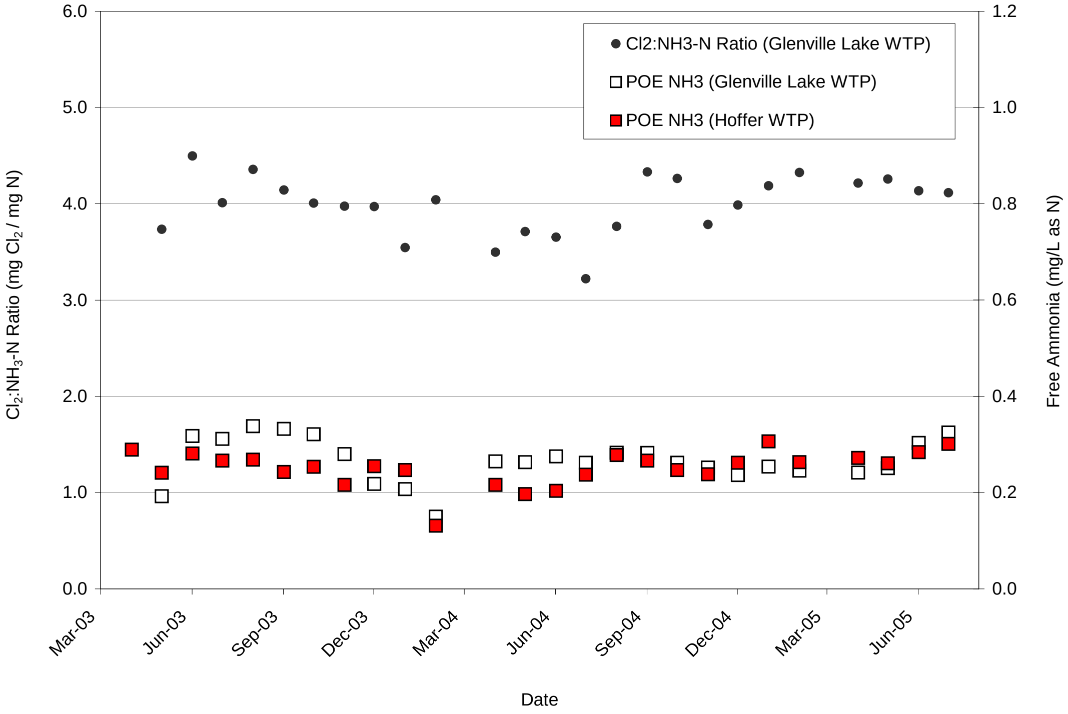
The monthly average combined chlorine concentrations at the POE to the distribution system from the Hoffer WTP and the Glenville Lake WTP are shown in Figure 4.9. Although the chloramine concentrations were consistent between the two plants in any given month, the values at each plant varied considerably throughout the period of analysis and generally followed a seasonal pattern, with peak concentrations occurring in the summer or early fall. The monthly average chloramine concentrations ranged from 2.5 to 4.5 mg/L, and the two-plant average over the 2.5-year period was 3.6 mg/L.

Figure 4.9: Monthly average combined chlorine concentrations at the point of entry to the distribution system from the Hoffer and Glenville Lake Water Treatment Plants (Fayetteville)



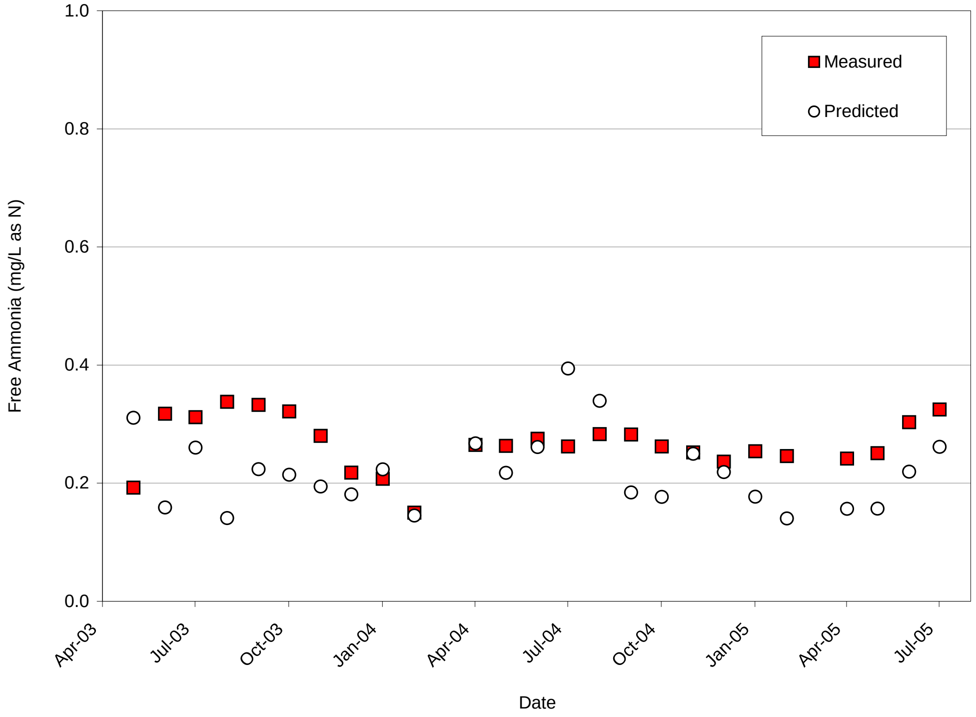
The Cl_2:NH_3-N ratios used to form monochloramine at the Glenville Lake WTP are shown in Figure 4.10. (This analysis could not be performed for the Hoffer WTP due to lack of free chlorine residual data at the PAA that were necessary to determine the total concentration of free chlorine present at the PAA, as indicated in Table 4.2.) The ratios were calculated using Equations *3.3* and *3.4*. The monthly average Cl_2:NH_3-N weight ratios ranged from 3.2:1 to 4.5:1, and the plant average over the 2.5-year period of analysis was 4.0:1. The ratios did not follow the strong seasonal pattern exhibited by the concentrations of combined chlorine at the POE (see Figure 4.9). This finding indicates that the utility made adjustments to the ammonia feed that dampened the effect of highly variable disinfectant concentrations on the Cl_2:NH_3-N ratios. Also shown in Figure 4.10 are the free ammonia concentrations at each treatment plant's POE. The monthly average values were consistent between the two plants and ranged from 0.13 to 0.32 mg/L, averaging 0.26 mg/L over the 2.5-year period.

Figure 4.10: Monthy average chlorine-to-ammonia ratios at the Glenville Lake Water Treatment Plant and monthly average free ammonia concentrations at the point of entry to the distribution system from the Hoffer and Glenville Lake Water Treatment Plants (Fayetteville)



Because the Cl_2:NH_3-N weight ratios used at the Glenville Lake WTP were consistently below the 5:1 theoretically optimum value, excess ammonia was expected to enter the distribution system. The predicted POE free ammonia concentrations were calculated using Equations *3.6* and *3.7* and are shown in Figure 4.11, along with the POE free ammonia concentrations measured by the utility. The predicted and measured free ammonia values average 0.22 mg/L and 0.27 mg/L, respectively, and follow a similar pattern over the period of analysis.

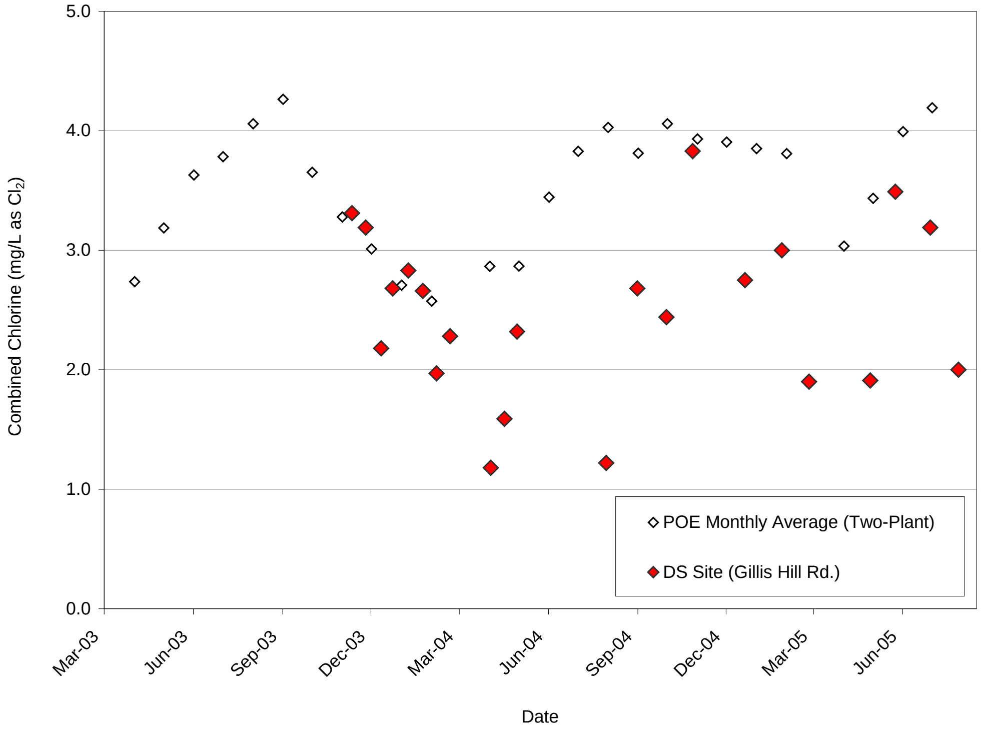
Figure 4.11: Monthly average predicted and monthly average measured free ammonia concentrations at the point of entry to the distribution system from the Glenville Lake Water Treatment Plant (Fayetteville)



The average pH values at the POE to the distribution system from the Hoffer WTP and Glenville Lake WTP over the 2.5-year period of analysis were each 7.4, with a standard deviation at each plant of 0.1. The average TOC concentrations at the POE from the Hoffer and Glenville Lake WTPs over the same period were 3.7 mg/L and 3.3 mg/L, respectively, with standard deviations of 1.2 mg/L and 1.1 mg/L. A one-month switch to free chlorine was made in March of each year following the year in which chloramination began.

Of the 11 distribution system sites identified by the utility as most vulnerable to nitrification, only Gillis Hill Road experienced recurring low chloramine residuals that do not appear to be attributable to unusually low chloramine concentrations at the POE or to a recent switch back to chloramines from free chlorine. The combined chlorine values for all samples taken at Gillis Hill Road over the period of analysis are plotted in Figure 4.12, along with the two-plant monthly average combined chlorine values at the POE. Approximately one third of all Gillis Hill Road samples had combined chlorine concentrations at or below 2 mg/L, with values as low as 1.2 mg/L. The low disinfectant residuals found at this site are consistent with the estimated HRT information provided, which indicates that the average water age at Gillis Hill Road (four to seven days) is the highest among the 11 sites for which data were provided.

Figure 4.12: Combined chlorine concentrations at Gillis Hill Road distribution system site and the two-plant monthly average combined chlorine concentrations at the point of entry to the distribution system (Fayetteville)



The low disinfectant residuals suggest that this site may be vulnerable to nitrification. However, due to limited data availability, it was not possible to determine whether or not the low residuals corresponded to other indicators of nitrification. The nitrite and nitrate measurements reported by Fayetteville included numerous unrealistic values (e.g. nitrite concentrations on the order of 3.0 mg/L), and the utility advised excluding these measurements from the analysis (Smith 2006). Thus, as indicated in Table 4.2, the data necessary to calculate changes in nitrite, nitrate, ammonia, DO, or pH were unavailable at either the POE or in the DS, or both. Additionally, the HPC data provided were quite limited for the 11 sites and typically did not correspond to sampling dates for which combined chlorine residual data were provided, thereby precluding analysis of the relationship between HPC and disinfectant residual. Further, no HPC data were provided for the Gillis Hill Road location.

4.3 GREENVILLE

A summary of the system data provided by Greenville is shown in Table 4.3.

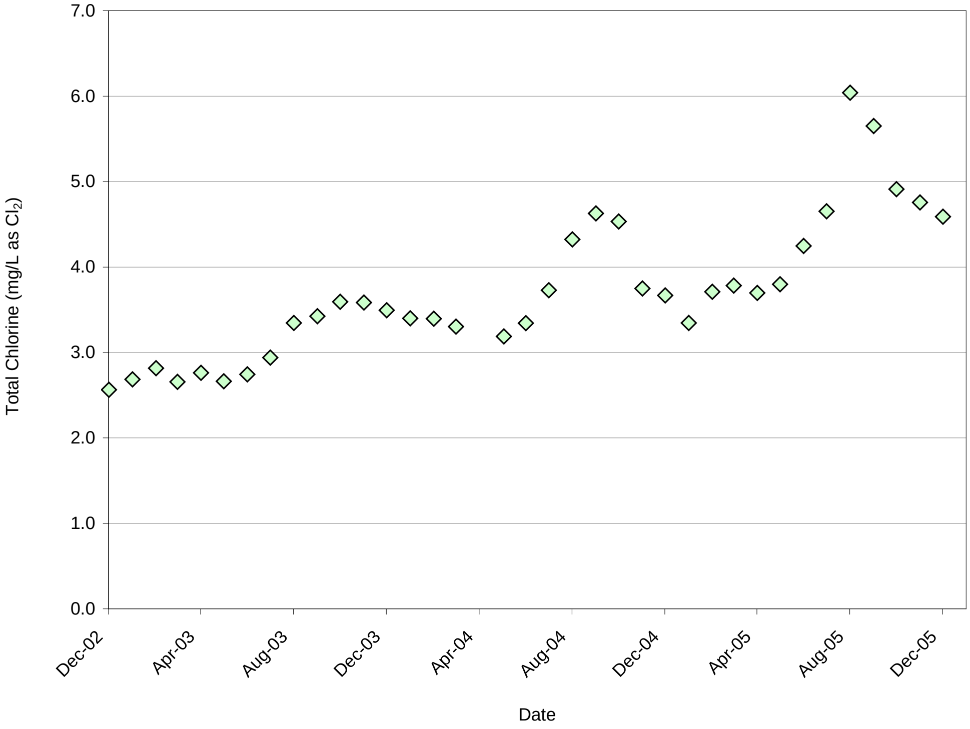
Table 4.3: Summary of system data provided (Greenville)

SYSTEM LOCATION	PERIOD	INFORMATION PROVIDED	
Point of NH_3 Addition (PAA)	12/02 - 12/05	Free Cl_2 (Before NH_3)	✓
		Add'l Cl_2 Dosed (w/ NH_3)	✓
		NH_3 Dosed	✓
Point of Entry (POE)	12/02 - 12/05	Daily Temp. (Raw Water)	✓
		Avg. Daily Total Cl_2	✓
		Daily pH	✓
		Total NH_3 (5x Weekly)	✓[1]
		NO_2^-	–
		NO_3^- (2x Weekly)	✓
		DO (5x Weekly)	✓[2]
		TOC (2x Weekly)	✓
Distribution System (DS)	1/03 - 12/05	Total Cl_2	✓
		Free Cl_2	✓[3]
		pH	✓
		Total NH_3	✓[3, 4]
		$NO_2^- + NO_3^-$	✓[3, 4]
		HPC	✓
		DO	✓[3]
		Approximate Water Age	–

[1] Parameter available beginning August 2003; [2] Parameter available beginning September 2004;
[3] Parameter not available prior to June/July 2005; [4] Data provided not used due to analytical discrepancy between POE and DS

The monthly average total chlorine concentrations at the POE to the distribution system are shown in Figure 4.13. The monthly average total chlorine residuals ranged from 2.5 to 6.0 mg/L, with a 3-year average value of 3.7 mg/L. The concentrations varied considerably, and generally increased over the period of analysis. The reason for this increasing trend is not known. The high total chlorine concentrations at the POE indicate that the utility may be vulnerable to violations of the 4.0 mg/L (as Cl_2) maximum residual disinfectant level (MRDL) established by Stage 1 of the D/DBP Rule. Indeed, the data provided indicate that 32% of 1044 samples taken at various sites throughout the distribution system during 2005 had total chlorine residuals at or above 4.0 mg/L. Further, the data indicate that 50% percent of the 439 distribution system samples taken between August and December 2005 (a period marked by consistently high total chlorine concentrations at the POE) had total chlorine residuals at or above 4.0 mg/L.

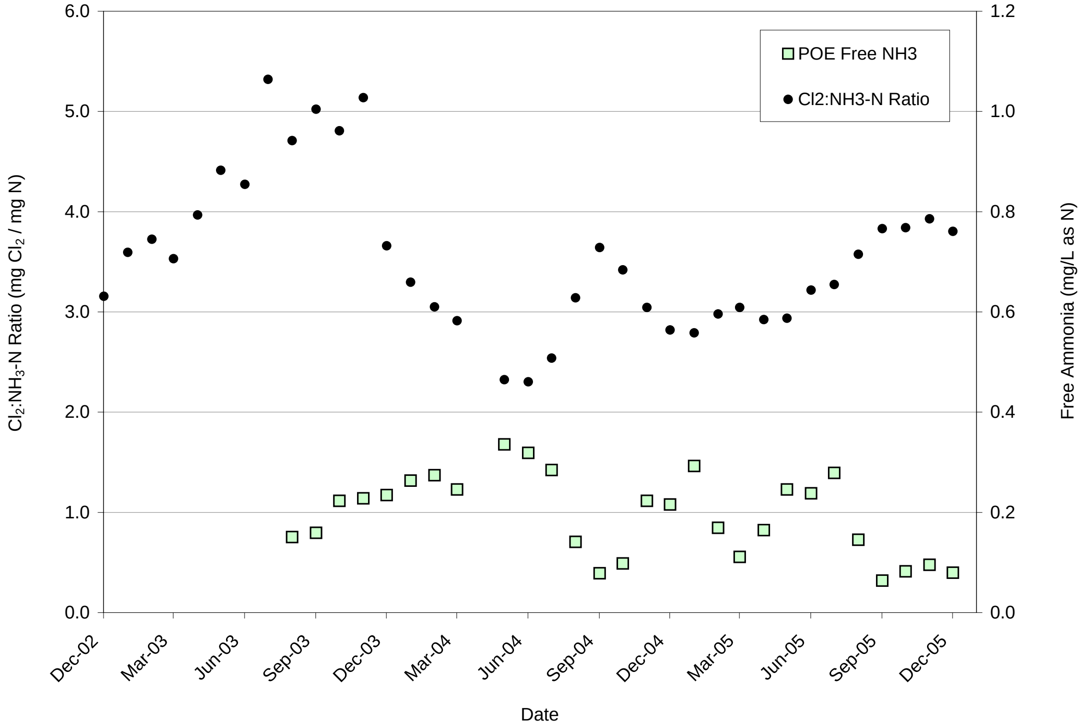
Figure 4.13: Monthly average total chlorine concentrations at the point of entry to the distribution system (Greenville)



The Cl_2:NH_3-N ratios used to form monochloramine were calculated using Equations *3.3* and *3.4*, and the results are shown in Figure 4.14. The monthly average Cl_2:NH_3-N weight ratios varied between 2.3:1 and 5.3:1, with ratios in recent years consistently below 5:1. The plant average over the 3-year period of analysis was 3.6:1. (It should be noted that the ammonia dosages used to calculate these ratios were approximated by the utility using pounds of ammonia dosed and the daily filter effluent volume in lieu of the actual volume of water to which ammonia was added.) During 2004 and 2005, the Cl_2:NH_3-N ratios followed a pattern similar to that exhibited by the POE total chlorine residuals shown in Figure 4.13 (e.g. peak values in the fall and low values in the spring). This finding indicates that adjustments to the ammonia feed that better reflect changing free chlorine concentrations at the PAA will help to stabilize the plant's Cl_2:NH_3-N ratios.

Figure 4.14 also shows the free ammonia concentrations at the POE, which were calculated (using Equations *3.1* and *3.2*) from the total ammonia concentrations measured by the utility. (The free ammonia concentrations at the POE were not provided.) The monthly average free ammonia concentrations varied between 0.06 and 0.34 mg/L, with an average value of 0.20 mg/L. The data represented in Figure 4.14 demonstrate the inverse relationship between the Cl_2:NH_3-N ratio and excess free ammonia; the further the Cl_2:NH_3-N weight ratio was from the theoretically optimum 5:1 ratio, the greater was the excess free ammonia concentration. These data suggest that increasing the Cl_2:NH_3-N ratios currently employed at the plant will reduce the introduction of free ammonia into the distribution system.

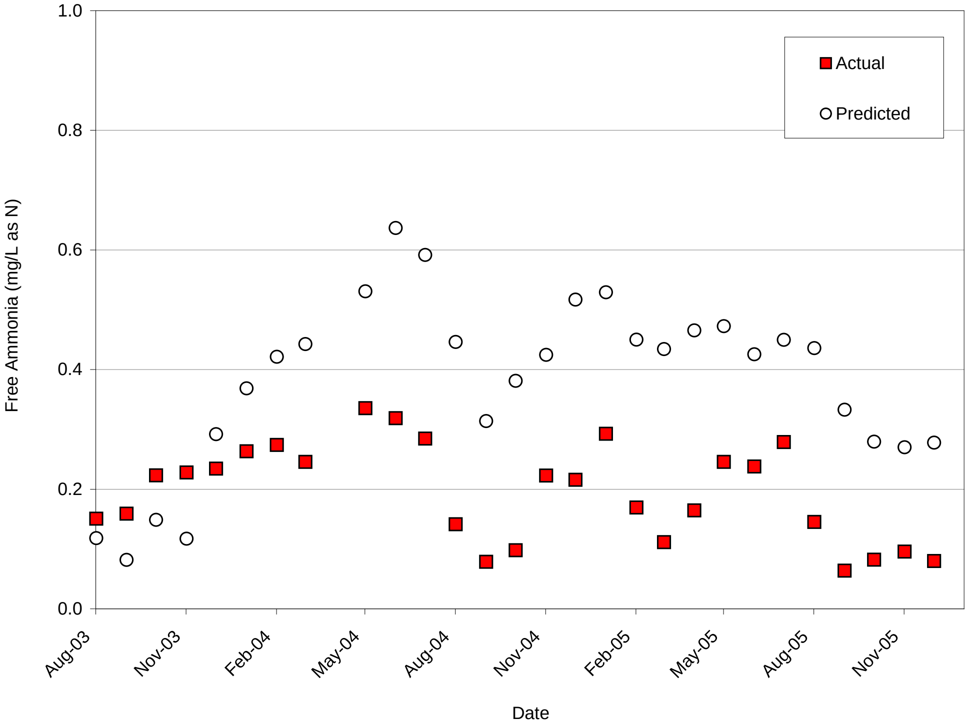
Figure 4.14: Monthly average chlorine-to-ammonia ratios and monthly average free ammonia concentrations at the point of entry to the distribution system (Greenville)



During this study, Greenville measured total ammonia concentrations in the raw water and immediately prior to the PAA on several occasions to test the validity of the assumption that any raw-water ammonia is oxidized during pretreatment and therefore does not contribute to the ammonia concentration available for chloramine formation (see Section 3.3). As shown in Table A.1 (see Appendix), these data suggest that a significant portion of the raw-water ammonia may be present at the PAA. It is not clear why this would be the case, as the free chlorine and ozone used by the plant for oxidation and primary disinfection would be expected to oxidize the ammonia. If ammonia introduced from the source water is in fact present at the PAA, Equation *3.4* will lead to an overestimate of the true $Cl_2:NH_3$-N ratios.

The predicted values of excess free ammonia were determined using Equations *3.5* and *3.6* and are plotted against the actual POE free ammonia concentrations in Figure 4.15. (The actual free ammonia concentrations at the POE were calculated from the concentrations of total ammonia measured at the POE, as previously noted.) The two sets of values follow a similar pattern, offering further evidence that increasing the $Cl_2:NH_3$-N ratios will reduce free ammonia concentrations at the POE. However, the predicted values are generally higher than the actual values by approximately 0.20 mg/L. The predicted and actual POE free ammonia concentrations average 0.40 mg/L and 0.20 mg/L, respectively, over the period of analysis. The reason for the discrepancy between these two sets of values is unknown.

Figure 4.15: Monthly average predicted and monthly average actual free ammonia concentrations at the point of entry to the distribution system (Greenville)



The average pH value at the POE to the distribution system over the 3-year period of analysis was 7.7, with a standard deviation of 0.1. The average TOC concentration at the POE over the same period was 3.3 mg/L, with a standard deviation of 0.6 mg/L. A one-month switch to free chlorine was made only during April of 2004.

Of the 283 distribution system sampling sites for which water quality data were provided, total chlorine residual values below 2 mg/L were measured at only 23 sites, and the majority of these low residuals appear to be a result of low total chlorine concentrations at the POE. The sites that appear most vulnerable to appreciable disinfectant loss are sites 15S and 16S, although few samples were taken at these sites over the period of analysis. The total chlorine concentrations for all samples taken at site 15S (3 samples) and site 16S (5 samples) are plotted in Figures 4.16 and 4.17, respectively, along with the monthly average total chlorine concentrations at the POE. Most of the samples taken at these sites had total chlorine residuals at or below 2 mg/L, with several values at or below 1 mg/L. Given the low sampling frequency at these sites (one or two times per year), however, it was not possible to determine the extent to which disinfectant loss was experienced at these locations during the full period of analysis.

Figure 4.16: Total chlorine concentrations at distribution system site 15S and monthly average total chlorine concentrations at the point of entry to the distribution system (Greenville)

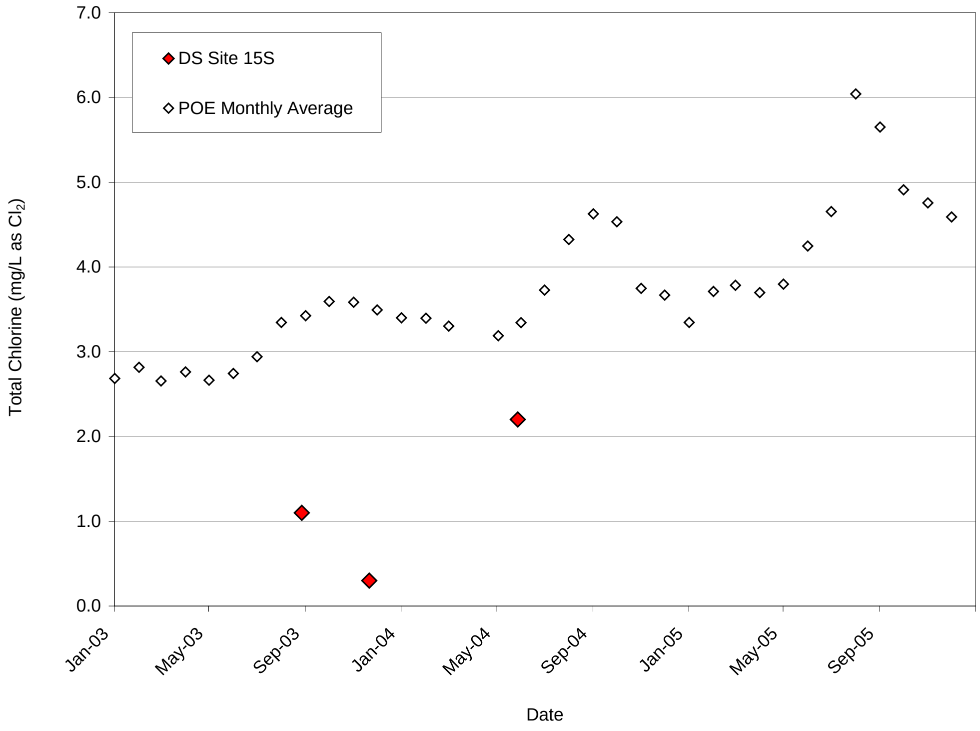
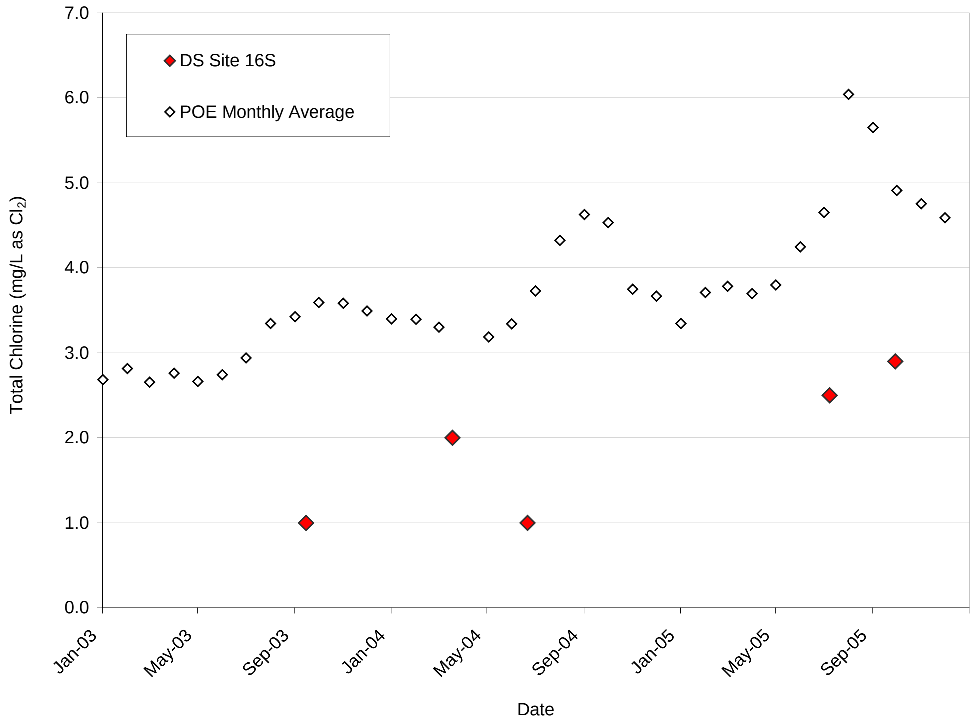


Figure 4.17: Total chlorine concentrations at distribution system site 16S and monthly average total chlorine concentrations at the point of entry to the distribution system (Greenville)



As indicated in Table 4.3, the utility began collecting distribution system data appropriate for monitoring nitrification (nitrite/nitrate, total ammonia, and DO concentrations) in the summer of 2005. The 234 sites at which these parameters were measured were evaluated for increases in the sum of nitrite and nitrate concentrations, as well as for decreases in total ammonia and DO concentrations. Despite high total chlorine residuals (an average of 3.8 mg/L) at all sites sampled between June and December 2005, losses in total ammonia concentration averaging 0.43 mg/L were detected in 99% of the samples. These losses in total ammonia concentration are suggestive of nitrification, and were expected to have been accompanied by increases in the sum of nitrite and nitrate concentrations. However, decreases in the sum of nitrite and nitrate concentrations averaging 1.22 mg/L were detected in all samples. (It should be noted that these losses reflect a comparison between the sum of the nitrite and nitrate concentration measured in the distribution system and the values of only nitrate measured at the POE.) These findings are at odds with one another, as they imply a net loss of nitrogen in the system. Subsequent investigation into this discrepancy revealed that the POE samples were analyzed for nitrite/nitrate and ammonia concentrations at the WTP laboratory, while the distribution system samples were analyzed for these parameters at the wastewater treatment plant (WWTP) laboratory (Chadwick 2006). To test for consistency between laboratory measurements, fifteen duplicate samples were collected by the utility for nitrite/nitrate and total ammonia measurement by each of the two laboratories. The results are shown in Table A.2 (see Appendix). The two sets of measurements differed considerably, particularly the nitrite/nitrate concentrations. Because the discrepancies were not systematic and thus did not permit the application of a correction factor to allow for comparison of the two sets of data, it was determined that the nitrogen data provided by the utility could not be used to identify nitrification episodes.

The HPC data were not well correlated with low total chlorine residuals measured at the 283 sampling sites for which data were provided, nor were changes in pH between the POE and the distribution system. In the absence of nitrogen data, these parameters offered little insight into nitrification detection. The magnitude and variability of the DO concentrations measured at the POE were considerable, ranging from 10 to 25 mg/L in as little as two days. The high DO concentrations were a result of Greenville's use of ozone as an oxidant. The large variability in DO did not allow for detection of the relatively small decreases in DO concentration expected to result from nitrification.

4.4 OWASA

A summary of the data provided by OWASA is shown in Table 4.4.

Table 4.4: Summary of system data provided (OWASA)

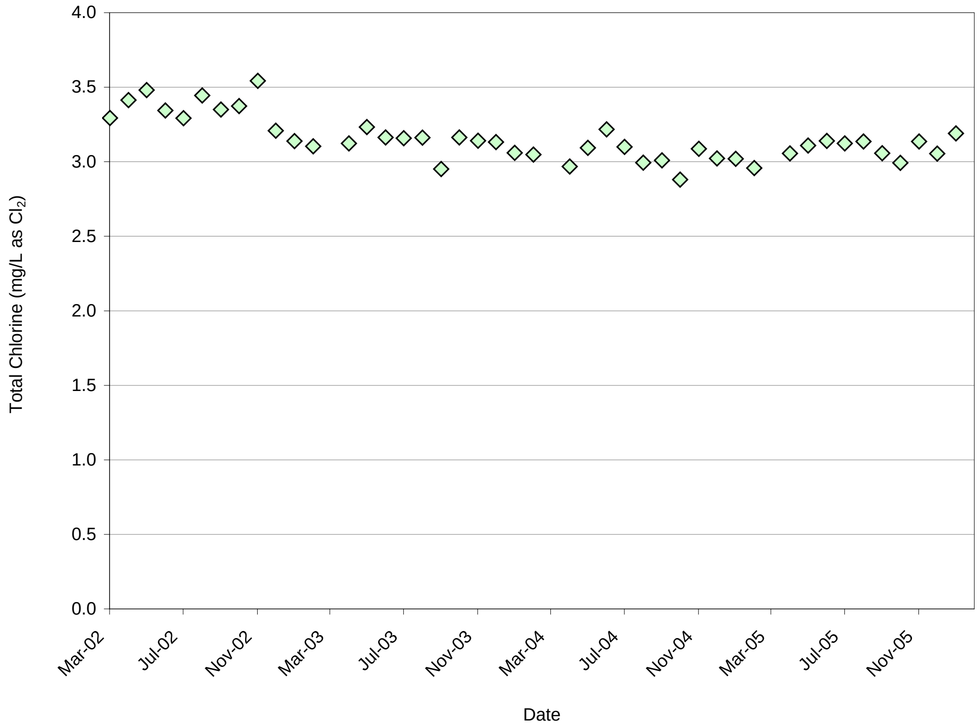
SYSTEM LOCATION	PERIOD	INFORMATION PROVIDED	
Point of NH_3 Addition (PAA)	3/02 - 1/06	Free Cl_2 (Before NH_3)	✓
		Add'l Cl_2 Dosed (w/ NH_3)	✓
		NH_3 Dosed	✓
Point of Entry (POE)	3/02 - 1/06	Daily Temp. (Raw Water)	✓
		Min. Daily Total Cl_2	✓[1]
		Daily pH	✓
		Weekly Free NH_3	✓[2]
		Weekly NO_2^-	✓[3]
		Weekly NO_3^-	✓[2]
		DO	–
		TOC (1-2x Weekly)	✓[4]
Distribution System (DS)	2/02 - 1/06	Total & Free Cl_2	✓
		pH	✓
		Free NH_3	✓[2]
		NO_2^-	✓[2]
		NO_3^-	✓[2]
		HPC	✓
		DO	-
		Approximate Water Age	✓

[1] Minimum daily POE Cl_2 residuals provided (average daily values not available);

[2] Parameter not available prior to November 2005; [3] Parameter available beginning August 2003; [4] Parameter available until July 2005

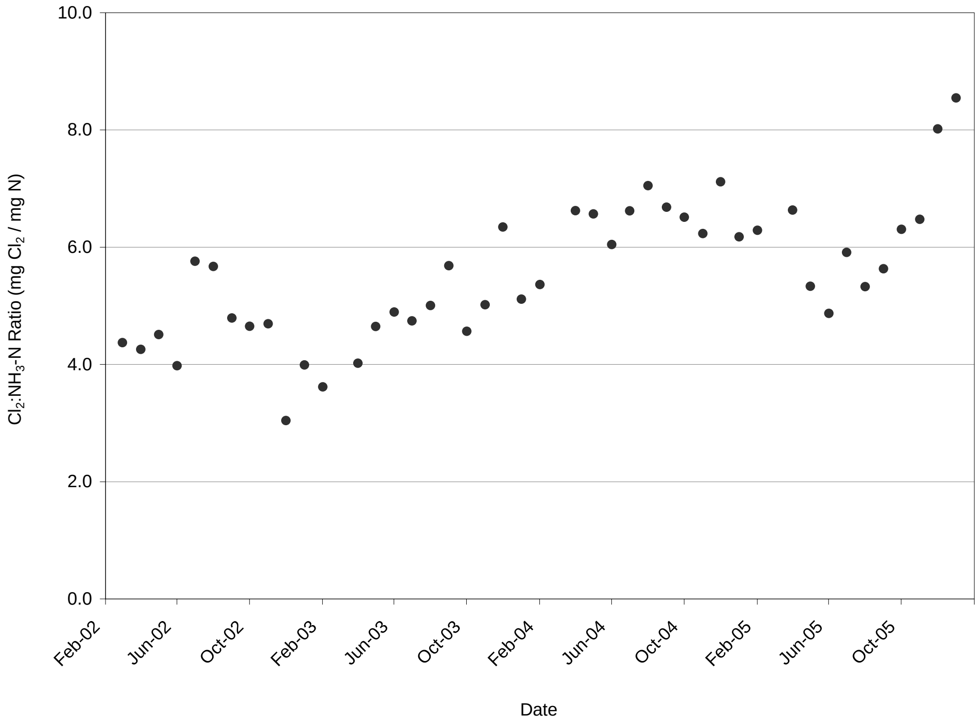
The monthly average total chlorine concentrations at the POE to the distribution system are shown in Figure 4.18. The concentrations were quite uniform, with monthly average values ranging from 2.9 to 3.5 mg/L, and a 4-year average value of 3.2 mg/L.

Figure 4.18: Monthly average total chlorine concentrations at the point of entry to the distribution system (OWASA)



The Cl_2:NH_3-N ratios used to form monochloramine were calculated using Equations *3.3* and *3.4*, and the results are shown in Figure 4.19. The ratios were highly variable and generally increased over the period of analysis. The monthly average ratios ranged from 3.0:1 to 8.6:1, and the 4-year average was 5.5:1. (It should be noted that the ammonia dosages used to calculate the Cl_2:NH_3-N ratios were approximated by the utility using pounds of ammonia dosed and the daily raw water volume in lieu of the actual volume of water to which ammonia was added. Thus, the true ammonia dosages should be higher than those reported by the utility, and the true Cl_2:NH_3-N ratios should be somewhat lower than those shown in Figure 4.19.)

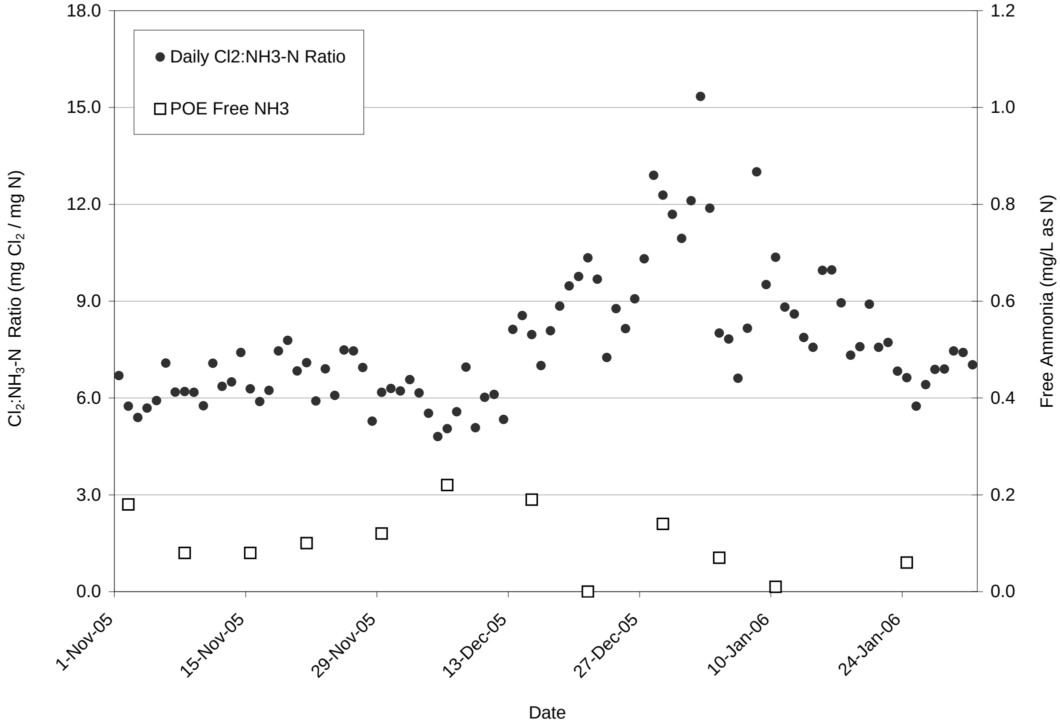
Figure 4.19: Monthly average chlorine-to-ammonia ratios (OWASA)



During this study, OWASA measured free and total ammonia concentrations in the raw water and immediately prior to the PAA on several occasions to test the validity of the assumption that any raw-water ammonia is oxidized during pretreatment and therefore does not contribute to the ammonia concentration available for chloramine formation (see Section 3.3). The results of these measurements are shown in Table A.3 (see Appendix). While most raw-water samples contained ammonia concentrations below the detection limit, samples collected on 5/31/06 and 6/21/06 contained detectable ammonia concentrations. Ammonia measurements just prior to the PAA on these dates suggest that pretreatment indeed removed the raw-water ammonia, thereby supporting the assumption that the only ammonia available for chloramine formation is that which is dosed at the PAA.

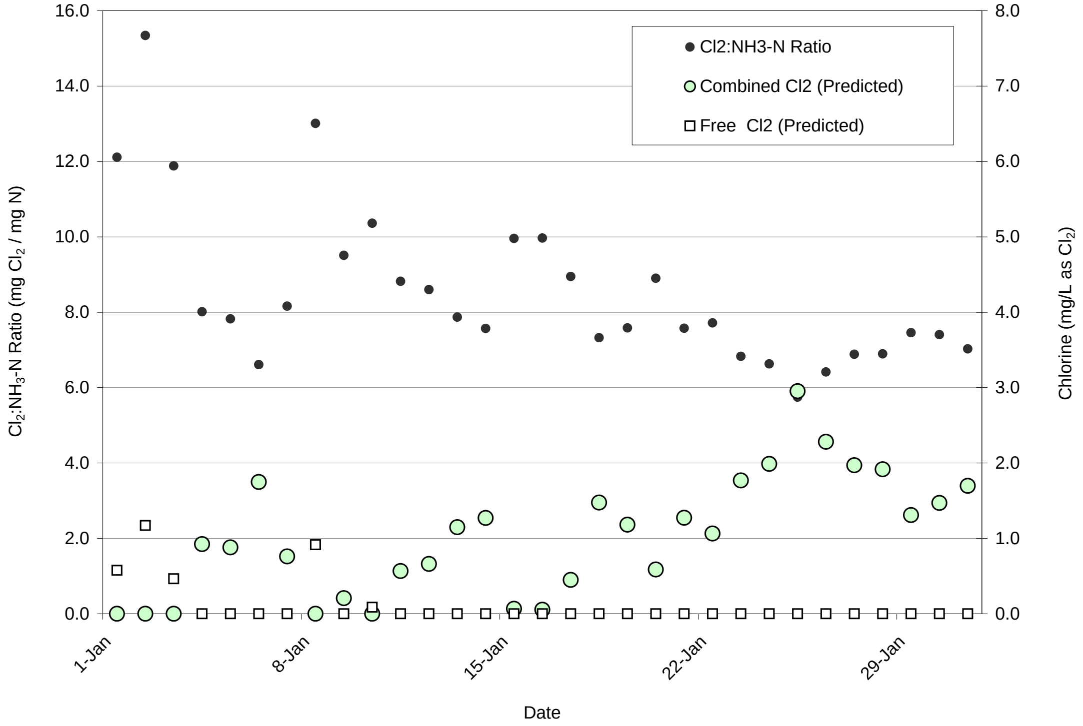
Because POE free ammonia data were not available prior to November 2005 (as indicated in Table 4.4), the monthly average free ammonia concentrations are not shown in Figure 4.19. Instead, each POE free ammonia measurement provided since November 2005 is plotted in Figure 4.20, along with the corresponding daily Cl_2:NH_3-N weight ratio. The daily Cl_2:NH_3-N ratios over the 3-month period for which POE free ammonia data were provided were generally extremely high, ranging from 4.8:1 to 15.3:1 and averaging 7.7:1. Therefore, little or no free ammonia would be expected to have entered the distribution system. However, the free ammonia concentrations measured at the POE ranged from 0 to 0.22 mg/L, with an average concentration of 0.10 mg/L.

Figure 4.20: Daily chlorine-to-ammonia ratios and free ammonia concentrations at the point of entry to the distribution system (OWASA)



The unusually high Cl_2:NH_3-N ratios calculated for OWASA would be expected to result in appreciable excess free chlorine that would act to destroy chloramine residual through breakpoint reactions (see Section 2.1.1). As an illustration, the theoretical (predicted) daily combined and free chlorine concentrations at the POE were calculated (using Equations *3.7 - 3.9*) during the month of January 2006. These values are plotted in Figure 4.21, along with the corresponding Cl_2:NH_3-N ratios. This plot demonstrates the inverse relationship between Cl_2:NH_3-N weight ratios above 5:1 and the combined chlorine residual concentration. If Cl_2:NH_3-N ratios are sufficiently high, the combined chlorine may be completely oxidized through breakpoint reactions, leaving only a free chlorine residual behind. Figure 4.21 demonstrates that Cl_2:NH_3-N ratios at OWASA were, theoretically, sufficiently high to bring the system beyond the breakpoint on five days in early January.

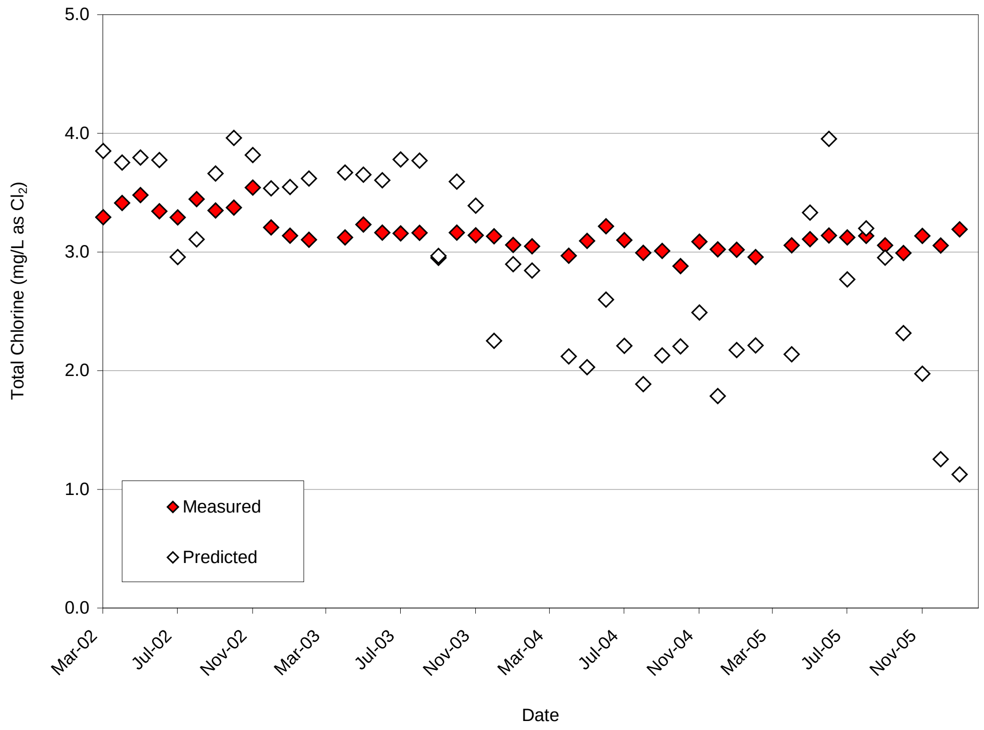
Figure 4.21: Daily chlorine-to-ammonia ratios and daily predicted free and combined chlorine concentrations at the point of entry to the distribution system (OWASA)



Despite the highly variable Cl_2:NH_3-N ratios shown in Figure 4.21, the total chlorine concentrations measured at the POE were quite consistent and did not follow the pattern predicted by the breakpoint calculations. Figure 4.22 illustrates the discrepancy between predicted and measured monthly average total chlorine concentrations at the POE. This disparity is most pronounced in 2004 and 2005. Although the difference may be due in part to the approximation of ammonia dosages using daily raw water flows (noted above), the discrepancy is too great to be attributed to this approximation alone. Rather, the data suggest that the finished water at OWASA exerts an appreciable free chlorine demand, thus leaving little excess free chlorine available for breakpoint reactions. While a breakpoint Cl_2:NH_3-N weight ratio of 10:1 was assumed for the calculation of predicted total chlorine concentrations at the POE (as described in Section 3.3.1), it appears that the breakpoint in this particular water may occur at a higher ratio. Kirmeyer et al. (2004) report breakpoint Cl_2:NH_3-N weight ratios as high as 16:1 in certain waters; OWASA's finished water may also exert an unusually high free-chlorine demand, although it is not clear why this should be the case. The data suggest that the optimal Cl_2:NH_3-N weight ratio for this utility may not be the 5:1 theoretical target, but rather a higher ratio. This optimal ratio may vary with raw water quality and can be determined by routinely monitoring the free ammonia concentration at the POE.

The average pH value at the POE to the distribution system over the 4-year period of analysis was 8.4, with a standard deviation of 0.2. The average TOC concentration at the POE over the 3.5-year period for which TOC data were provided was 1.9 mg/L, with a standard deviation of 0.4 mg/L. A one-month switch to free chlorine was made in March of each year following the year in which chloramination began.

Figure 4.22: Monthly average predicted and monthly average measured total chlorine concentrations at the point of entry to the distribution system (OWASA)



Of the 165 distribution system sampling sites for which water quality data were provided, total chlorine residuals below 2 mg/L were measured at only 11 sites. Of these 11 sites, only sites A58 and B28 had recurring low residuals that do not appear to be a result of a recent switch back to chloramines from free chlorine. The estimated HRTs for sites A58 and B28 are four and eight days, respectively. The total chlorine concentrations for all samples taken at sites A58 and B28 during the period of analysis are plotted in Figures 4.23 and 4.24, respectively, along with the 4-year average total chlorine concentration at the POE. (The different time scales between Figures 4.23 and 4.24 should be noted.) One third of all samples taken at site A58 had total chlorine concentrations at or below 2 mg/L. Several samples taken at site B28 had total chlorine concentrations at or below 1.5 mg/L, and a value of 0.4 mg/L was measured in November 2003.

Figure 4.23: Total chlorine concentrations at distribution system site A58 and average total chlorine concentration at the point of entry to the distribution system (OWASA)

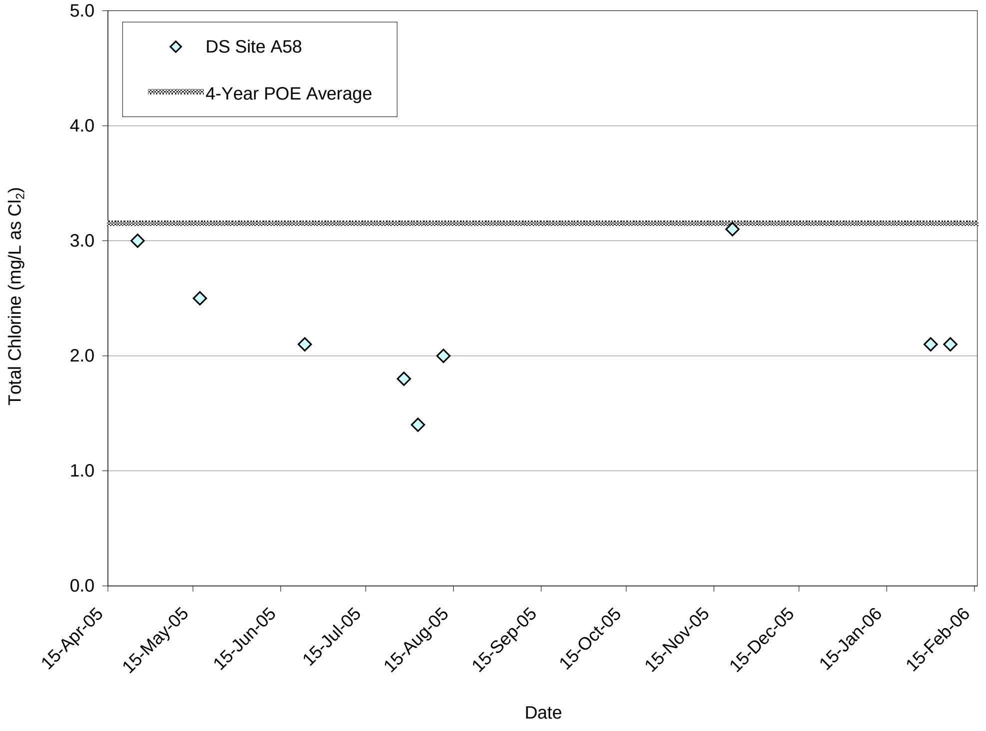
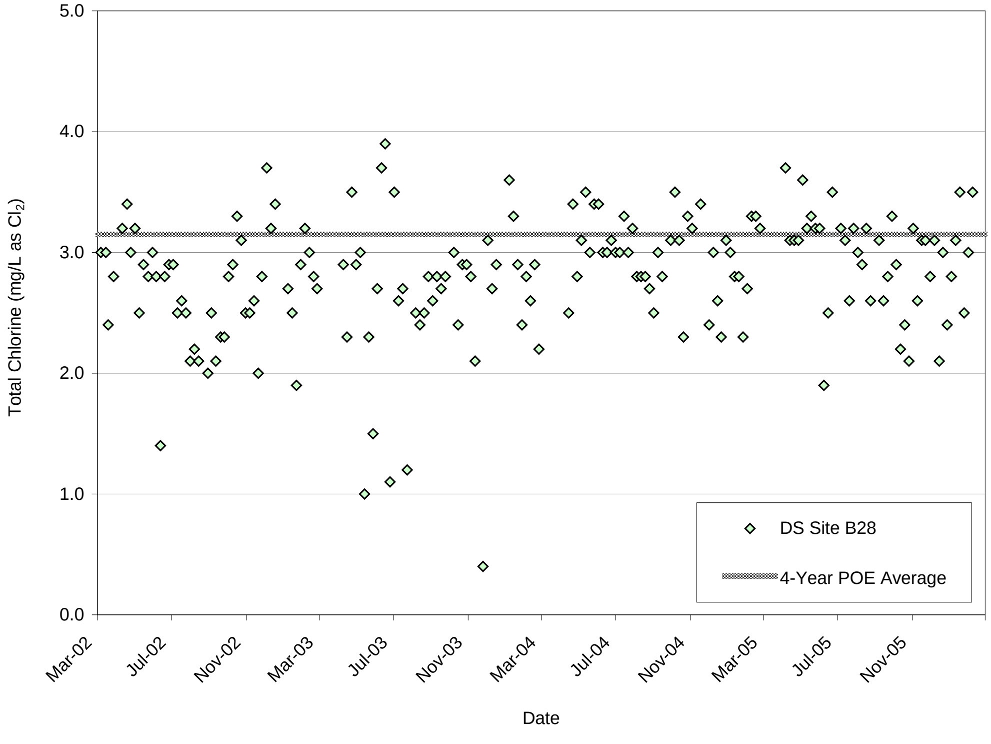


Figure 4.24: Total chlorine concentrations at distribution system site B28 and average total chlorine concentration at the point of entry to the distribution system (OWASA)



Nitrite, nitrate, and free ammonia data were provided for 38 sampling sites throughout the distribution system, including sites A58 and B28, from November 2005 to February 2006. (Prior to November 2005, these data were not collected.) Although water temperatures during this period typically do not favor nitrifying activity, these nitrogen data were analyzed for evidence of nitrification. The nitrite data do not suggest nitrification, as nitrite concentrations in the distribution system were below the detection limit of 0.10 mg/L in all samples collected. Total ammonia concentrations, calculated from free ammonia and total chlorine measurements, also do not suggest nitrification, as concentrations were consistent between the POE and the distribution system sampling sites. (The average change in total ammonia concentration was 0.00 mg/L, with a standard deviation of 0.07 mg/L.) Analysis of the nitrate data is inconclusive, as nitrate concentrations at the POE were too variable to accurately assess change between the plant and the distribution system. Nitrate values at the POE were found to vary between 0.5 and 1.4 mg/L within one week. Without accurate knowledge of the water age at each sampling site, change must be assessed using average concentrations at the POE. Therefore, the highly variable POE concentrations precluded accurate measurement of change.

HPC and pH data, which were available for all DS sampling sites for the full period of system analysis, offered little insight into nitrification occurrence. Both parameters were found to be poorly correlated with low total chlorine residual values.

4.5 RALEIGH

A summary of the treatment plant and distribution system data provided by Raleigh is shown in Table 4.5.

Table 4.5: Summary of system data provided (Raleigh)

SYSTEM LOCATION	PERIOD	INFORMATION PROVIDED	
Point of NH_3 Addition (PAA)	1/04 - 10/05	Free Cl_2 (Before NH_3)	✓
		Add'l Cl_2 Dosed (w/ NH_3)	–[1]
		NH_3 Dosed	✓
Point of Entry (POE)	1/02 - 10/05	Daily Temp. (Raw Water)	✓
		Min. Daily Total Cl_2	✓[2]
		Daily pH	✓
		Weekly Free NH_3	✓[3]
		NO_2^-	–
		Weekly NO_3^-	✓
		DO (5x Weekly)	✓[3]
		Daily TOC	✓[4]
Distribution System (DS)	5/02 - 2/06	Total & Free & Combined Cl_2	✓
		pH	✓
		Free NH_3	✓[5]
		NO_2^-	✓[5]
		NO_3^-	✓[5]
		HPC	✓
		DO	-
		Approximate Water Age	-

[1] No additional Cl_2 is dosed at the PAA; [2] Minimum daily POE Cl_2 residuals provided (average daily values not available); [3] Parameter available from July 2002 through August 2005; [4] Parameter available beginning July 2002; [5] Parameter available for 4 DS sites, and from February through August 2005 only

The monthly average total chlorine concentrations at the POE to the distribution system are shown in Figure 4.25. The monthly average values fluctuated between 3.0 and 4.1 mg/L, with a 4-year average value of 3.6 mg/L. The total chlorine concentrations generally followed a seasonal pattern, with peak concentrations typically occurring in the fall.

The Cl_2:NH_3-N ratios used to form monochloramine were calculated using Equations *3.3* and *3.4*. However, because Raleigh routinely adds ammonia at two different locations (at the outlet of each of two parallel clearwells), calculating the overall system Cl_2:NH_3-N ratios required an additional step compared to the other utilities. Because only the overall ammonia dosages were provided (in lieu of the ammonia dosages at each of the two PAAs), it was necessary to determine the daily weighted average of the free chlorine residuals at each of the two PAAs to calculate an overall system Cl_2:NH_3-N ratio. (Raleigh does not dose additional free chlorine at the PAAs.) Therefore, pumping records were obtained from the utility for a 2-year period in order to weight the free chlorine residuals provided according to the fraction of total daily flow passing through each of the two clearwells. The Cl_2:NH_3-N ratios calculated using the weighted averages of free chlorine residual are shown in Figure 4.26 for the 2-year period for which free chlorine residual and pumping/flow data were provided. The ratios were relatively consistent over the period of analysis, with monthly average values fluctuating between 3.5:1 and 4.2:1. With the exception of February 2004, all monthly average Cl_2:NH_3-N ratios were below 4.0:1, and the 2-year plant average was 3.8:1. These ratios are consistently higher than the 3.0:1 ratio established as the target by the utility (Forkner 2006). (It should be noted that the ammonia dosages provided by the utility were not used to calculate the Cl_2:NH_3-N ratios, as these concentrations were approximated by the utility using pounds of ammonia dosed and the daily raw water volume in lieu of the actual volume of water to which ammonia was added. Instead, the aforementioned pumping records were used to calculate the daily volume of ammoniated water and thus more precise ammonia dosages. These more precise ammonia dosages were used to determine the Cl_2:NH_3-N ratios shown in Figure 4.26.)

Also shown in Figure 4.26 are the free ammonia concentrations measured at the POE. These free ammonia values were unusually high and considerably variable, with monthly averages ranging from 0.29 to 0.95 mg/L, and a 3-year average value of 0.64 mg/L. Given the relative stability of the Cl_2:NH_3-N ratios, the reason for the high variability in free ammonia concentrations is not apparent.

Figure 4.25: Monthly average total chlorine concentrations at the point of entry to the distribution system (Raleigh)

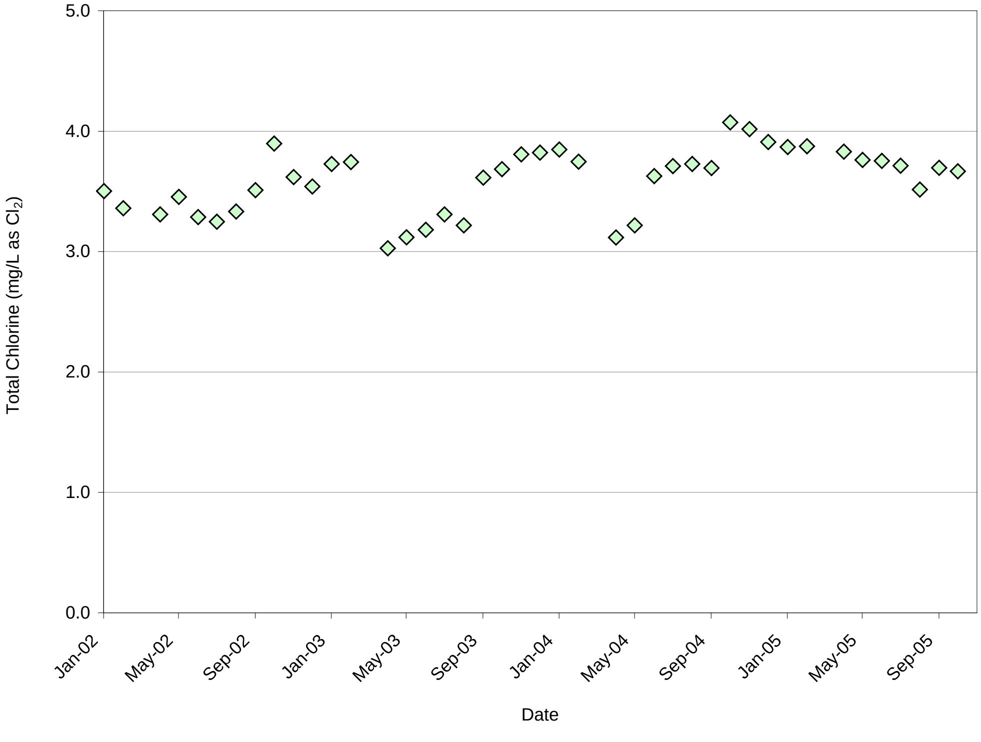
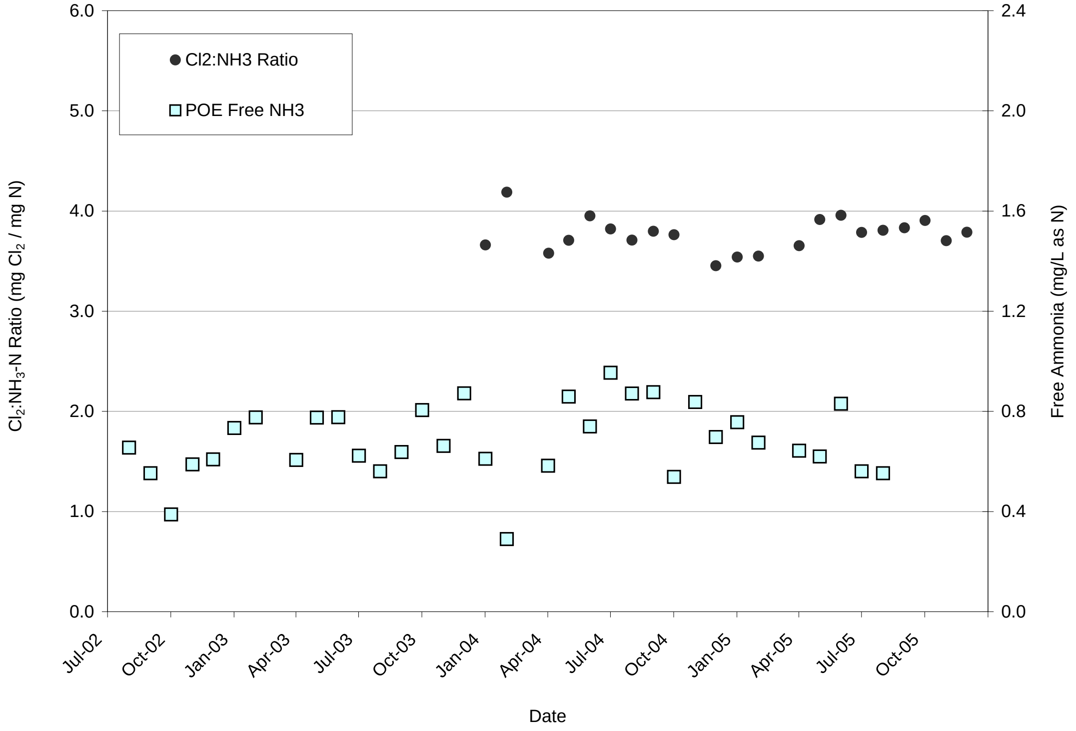
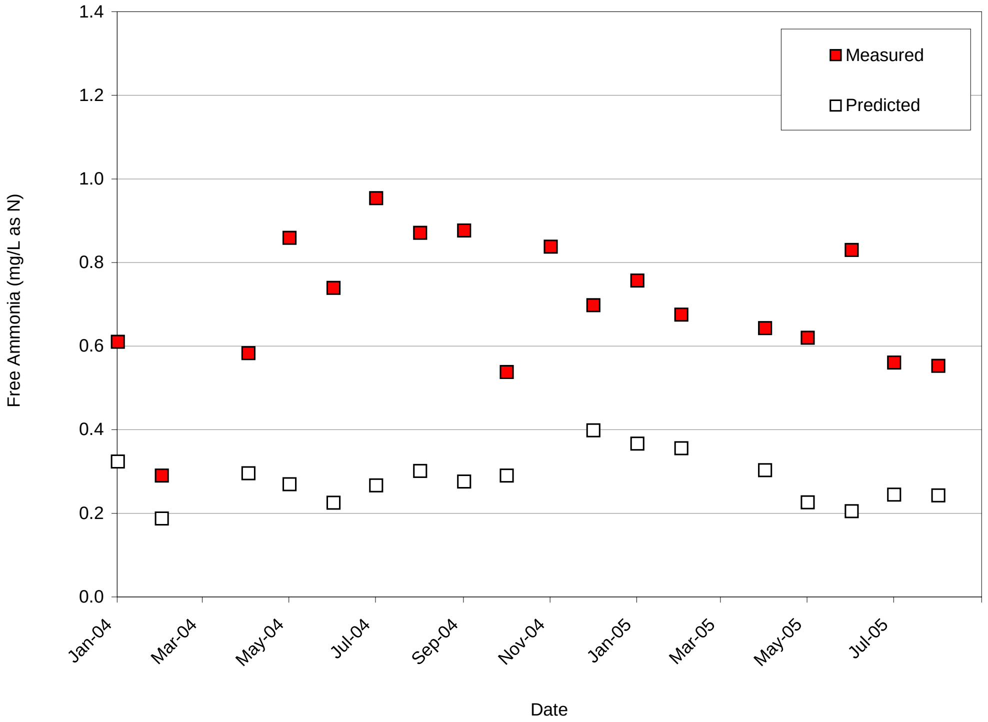


Figure 4.26: Monthly average chlorine-to-ammonia ratios and monthly average free ammonia concentrations at the point of entry to the distribution system (Raleigh)



Although a certain amount of free ammonia would be expected to enter Raleigh's distribution system due to the use of Cl_2:NH_3-N weight ratios consistently below the 5:1 theoretically optimum value, the free ammonia concentrations measured at the POE were well in excess of the expected concentrations. The predicted excess ammonia concentrations were calculated using Equations *3.5* and 3.*6*, and the discrepancy between the predicted and measured free ammonia concentrations is shown in Figure 4.27. The 2-year average predicted free ammonia concentration at the POE is 0.28 mg/L. Thus, the average measured value of 0.70 mg/L over this 2-year period is unexpectedly high. The average ammonia dosage at the PAA over this same period was 1.05 mg/L. Therefore, an average ammonia concentration at the POE of 0.70 mg/L implies that only 0.35 mg/L of free ammonia was consumed by the formation of monochloramine. Given the stoichiometry of monochloramine formation (5:1 mg Cl_2/mg N), the average concentration of combined chlorine formed under these conditions should have been approximately 1.8 mg/L. Any free chlorine available in excess of that used to form monochloramine should have acted to destroy the chloramine residual through the breakpoint reactions (see Section 2.1.1), thus further reducing the total chlorine concentration. However, the average total chlorine concentration at the POE during this 2-year period was 3.7 mg/L. Therefore, the high free ammonia concentrations measured at the POE do not appear to be consistent with the ammonia dosage and total chlorine residual data provided. Although the reason for the discrepancy between predicted and measured excess free ammonia concentrations is unknown, the data clearly indicate that an upward adjustment to the Cl_2:NH_3-N ratio should be made in order to achieve a lower concentration of free ammonia entering the distribution system.

Figure 4.27: Monthly average predicted and monthly average measured free ammonia concentrations at the point of entry to the distribution system (Raleigh)



The average pH value at the POE to the distribution system over the 4-year period of analysis was 8.5, with a standard deviation of 0.4. The average TOC concentration at the POE over the 3.5-year period for which TOC data were provided was 2.4 mg/L, with a standard deviation of 0.2 mg/L. A one-month switch to free chlorine was made in March of each year.

Of the 793 distribution system sampling sites for which water quality data were provided by the utility, total chlorine residuals below 2 mg/L were detected at 185 sites. The sites with the most recurring low disinfectant residuals are listed in Table 4.6. The total chlorine concentrations measured in all samples taken at two of the 13 sites listed in Table 4.6 (sites 210 and 390) are plotted in Figures 4.28 and 4.29, along with the 4-year average total chorine concentration at the POE. Approximately one half of the samples taken at these sites over the period of analysis had total chlorine concentrations at or below 1 mg/L. The most recent samples taken from these sites, however, indicate considerably more stable disinfectant residuals. This is also true for most sites listed in Table 4.6. The improved disinfectant stability can be attributed to structural and operational changes made by the utility. Several of the sites are located along what was once a dead-end service line, but a fairly recent service extension appears to have alleviated the problem of low total chlorine residuals at these sites (Hoyle 2006), presumably by decreasing the HRT. Additionally, the utility has instituted regular flushing at certain locations and has increased the chlorine concentration during the annual temporary switch to free chlorine (Hoyle 2006). It appears that these measures have met with success.

Table 4.6: Distribution system sites with recurring low total chlorine concentrations (Raleigh)

Site #	Site Address	% of Samples < or = 2 mg/L Total Chlorine	% of Samples < or = 1 mg/L Total Chlorine	Lowest Total Chlorine Value (mg/L)
077	2204/2208 Windy Woods Dr.	40%	20%	0.20
078	2209 Windy Woods Dr.	40%	20%	0.14
210	5830 Raynor Rd./301Hein Dr.	57%	50%	0.24
389	2205 Windy Woods Dr.	41%	35%	0.29
390	2337 Windy Woods Dr.	44%	38%	0.33
414	832 Purser Dr.	29%	21%	0.32
416	1602 Cranston Rd.	24%	24%	0.26
417	509 Longview St.	36%	21%	0.55
471	11208 N. Radner Way	27%	18%	0.70
599	3309 Byers Dr.	33%	25%	0.64
600	3204 Byers Dr.	33%	25%	0.41
628	207 Gipson Dr.	45%	27%	0.50
630	610 Rand Mill Rd.	36%	18%	0.87

Figure 4.28: Total chlorine concentrations at distribution site 210 and average total chlorine concentration at the point of entry to the distribution system (Raleigh)

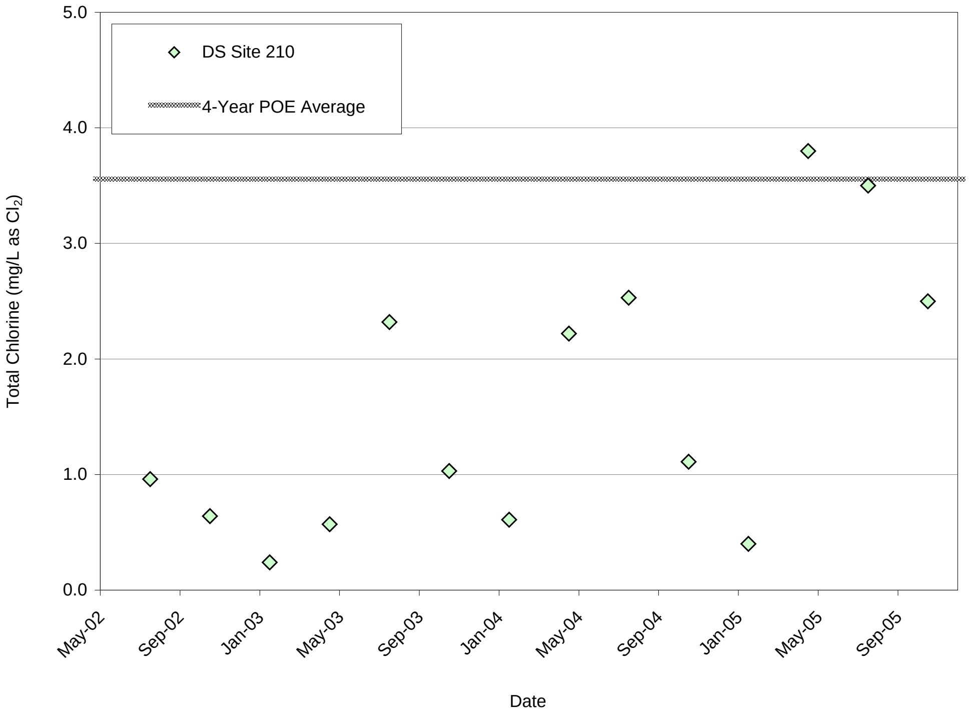
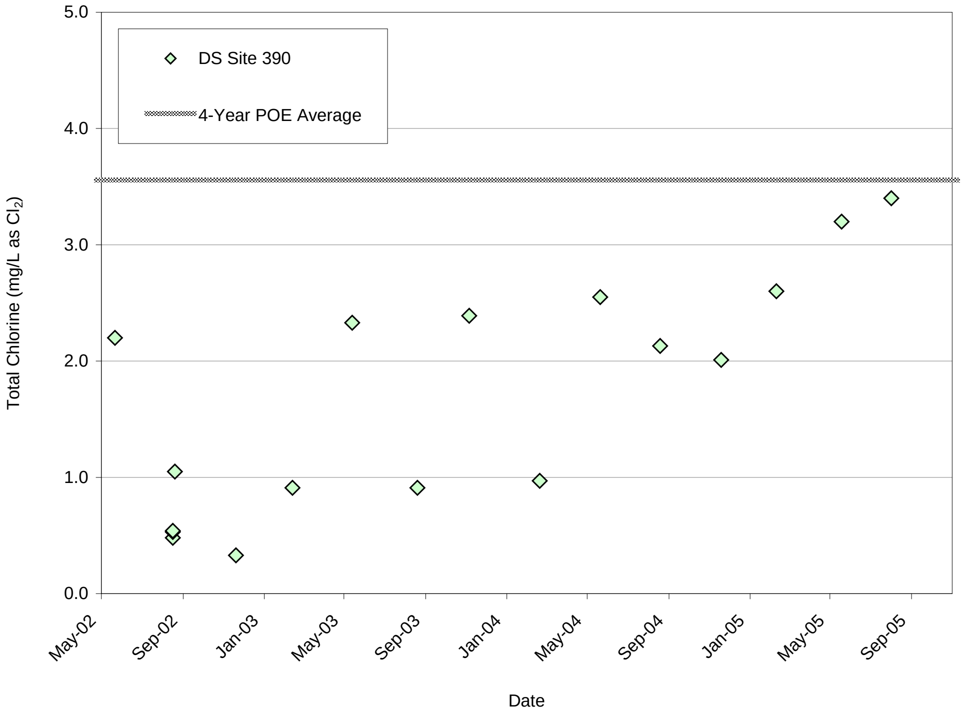


Figure 4.29: Total chlorine concentrations at distribution site 390 and average total chlorine concentration at the point of entry to the distribution system (Raleigh)



Although the low disinfectant residuals detected at numerous sites within Raleigh's distribution system may have been associated with episodes of nitrification, the utility did not routinely collect the nitrogen data necessary to assess nitrification occurrence (as indicated in Table 4.5). However, previous studies found evidence of nitrification within Raleigh's distribution system at a number of sites and on several occasions between 1997 and 2000 (DiGiano et al. 2000; DiGiano et al. 2002), indicating that the system is indeed vulnerable to nitrification. The high free ammonia concentrations introduced at the POE favor nitrifying activity, as do the long HRTs associated with larger distribution systems. Raleigh's distribution network, composed largely of iron pipe (CDM 2006), also adds to the system's vulnerability. This utility's potential for nitrification is also evidenced by sampling results from one of the satellite communities that purchases Raleigh's finished water, as shown in Table A.4 (see Appendix). These samples, collected in September of 2004, illustrate the decreasing total chlorine and ammonia concentrations and the increasing nitrite and nitrate concentrations associated with nitrification.

While Raleigh did not routinely collect the data necessary to identify nitrification occurrence, a study by CDM (2006) yielded nitrite, nitrate, and free ammonia data for four distribution system sites for the period from February to August 2005. The four sites were selected based upon their history of frequent coliform detections. Given that a number of the conditions that favor the growth of coliform bacteria also favor the growth of nitrifying bacteria, these sites were considered vulnerable to nitrification. However, the data collected by CDM suggest that nitrification did not occur at any of the four sites during the 7-month sampling period. Total chlorine concentrations were high at all sites, averaging 3.9 mg/L over the six months during which chloramines were used. Nitrite concentrations were below the detection limit of 0.10 mg/L in all samples except for those taken on February 10, and the high concentration detected at all four sites on this date were attributed to analytical error (CDM 2006). Nitrate concentrations remained stable between the plant and each of the four sites, and thus did not reflect nitrifying activity. Given the consistently high disinfectant residual maintained during the period of analysis and the lack of increased nitrite or nitrate concentrations, decreases in free ammonia concentrations suggestive of nitrification would not be expected. However, the data indicate considerable and consistent losses in free ammonia concentration between the POE and each of the sampling sites. These decreases in free ammonia concentration averaged 0.44 mg/L and were detected in all but one of the samples analyzed. Because the other data are not suggestive of nitrification, it appears that the decreases in free ammonia concentration observed at these four sampling sites may be a result of analytical uncertainty related to the unexpectedly high concentrations of free ammonia measured at the POE (see Figure 4.27 and related discussion).

The HPC and pH data provided for all sampling locations over the full period of analysis were not well correlated with total chlorine concentration and, in the absence of nitrogen data, offered little in the way of identifying nitrification episodes.

4.6 NDMA

4.6.1 Durham

NDMA measurements from October 12 and November 9, 2006 at Station E30 are displayed in Table 4.7. NDMA concentrations ranged from 3.8 ng/L to 11.3 ng/L on the two sampling dates.

While NDMA is not regulated in North Carolina at this time, some of the measured concentrations were close to, or slightly above, the Notification Level of 10 ng/L for California.

Table 4.7 NDMA Concentration at Durham Station E30

Date	Time	NDMA (ng/L)			
		Trial 1	Trial 2	Average	Standard Deviation
10/12/06	10:58	6.1	N/A*	6.1	N/A*
	13:58	11.3	9.6	10.5	1.20
	16:56	8.0	6.0	7.0	1.41
11/9/06	10:45	3.8	5.1	4.5	0.92
	13:44	6.0	5.9	6.0	0.07
	15:44	6.5	6.6	6.6	0.07

*Not Available

4.6.2 Raleigh

Several sites in Wendell, NC, a satellite system using Raleigh water, were analyzed for NDMA. For samples collected on October 30, 2006 at the Lions Club Road sampling station, the NDMA results are shown in Table 4.8. The concentration ranged from 5.9 ng/L to 7.6 ng/L. For various sites sampled on November 30, 2006, the NDMA results are shown in Table 4.9. The NDMA concentrations ranged from 4.2 ng/L to 6.8 ng/L. Despite the widespread reported occurrence of nitrification at these stations in Wendell, NDMA levels were below California's Notification Level, and there was little variation between sites.

Table 4.8 NDMA Concentration at Lions Club Road, Wendell, NC

Date	Time	NDMA (ng/L)			
		Trial 1	Trial 2	Average	Standard Deviation
10/30/06	9:23	5.9	N/A*	5.9	N/A*
	10:15	5.7	6.1	5.9	0.28
	11:15	7.6	7.2	7.4	0.28

*Not Available

Table 4 9 NDMA Concentration for Various Sites in Wendell, NC

Date	Site	Time	NDMA (ng/L)			
			Trial 1	Trial 2	Average	Standard Deviation
11/30/06	Lions Club Road	11:19	4.2	4.6	4.4	0.14
	Morphus Bridge Road & East 3rd Street	11:33	5.1	5.9	5.5	0.28
	1016 Morphus Bridge Road	12:32	6.8	6.2	6.5	0.21

4.7 SUMMARY AND DISCUSSION OF RESULTS

4.7.1 Data Availability

While the list of parameters requested from each utility (see Section 3.2) represents an optimal dataset for assessing nitrification potential and occurrence, a number of the requested parameters were not routinely measured by the utilities. Thus, the analyses performed in this study were limited by the data provided. A summary of the information provided by each utility is given in Table 4.10.

Table 4.10 Summary of system data provided by each utility

LOCATION	PARAMETER	UTILITY				
		Durham	Fayetteville	Greenville	OWASA	Raleigh
Point of NH_3 Addition (PAA)	Free Cl_2 (Before NH_3)	✓	✓[1]	✓	✓	✓
	Add'l Cl_2 Dosed (w/ NH_3)	–	✓	✓	✓	–[7]
	NH_3 Dosed	✓	✓	✓	✓	✓
Point of Entry (POE)	Temperature (Raw Water)	✓	✓	✓	✓	✓
	Total Cl_2	✓	–	✓	✓	✓
	Free Cl_2	–	–	–	–	–
	Combined Cl_2	–	✓	–	–	–
	pH	✓	✓	✓	✓	✓
	Free NH_3	✓	✓	–	✓[6]	✓
	Total NH_3	–	–	✓	–	–
	NO_2^-	–	–[2]	–	✓	–
	NO_3^-	✓	–[2]	✓	✓[6]	✓
	DO	✓	–	✓	–	✓
	TOC	✓	✓	✓	✓	✓
Distribution System (DS)	Total Cl_2	✓	✓	✓	✓	✓
	Free Cl_2	–	✓	✓[4]	✓	✓
	Combined Cl_2	–	✓	–	–	✓
	pH	–	–	✓	✓	✓
	Free NH_3	–	–	–	✓[6]	✓[8]
	Total NH_3	–	–	–[2, 4]	–	–
	NO_2^-	–	–[2]	–[2, 4, 5]	✓[6]	✓[8]
	NO_3^-	✓	–[2]	–[2, 4, 5]	✓[6]	✓[8]
	HPC	✓	✓[3]	✓	✓	✓
	DO	–	–	✓[4]	–	–
	Approximate Water Age	–	✓	–	✓	–

[1] Glenville Lake WTP only; [2] Data provided not used due to analytical inconsistencies; [3] Limited data provided; [4] Parameter not available prior to June/July 2005; [5] Sum of nitrite and nitrate provided; [6] Parameter not available prior to November 2005; [7] No additional chlorine dosed at the PAA; [8] Parameter available for 4 DS sites, and from February through August 2005 only

The data required to calculate the Cl_2:NH_3-N ratios were not available from all utilities. At the Hoffer WTP in Fayetteville, the free chlorine concentrations at the PAA were not routinely measured. Therefore, the Cl_2:NH_3-N ratios could not be calculated. The values of free chlorine dosed at the PAA were not provided for Durham's Brown WTP or Williams WTP; therefore the Cl_2:NH_3-N ratios could only be approximated by assuming that the total chlorine concentrations measured at the POE were equal to the total free chlorine concentrations at the PAA.. In Raleigh, the availability of only overall ammonia dosages (versus dosages at each of the two PAAs) did not allow for the calculation of the Cl_2:NH_3-N ratios at each PAA. Instead, only the plant average ratios could be calculated, which precluded the detection of potentially disparate ratios between the two PAAs. Therefore, this study found that some utilities may need to make adjustments to certain monitoring/recording practices to allow for the calculation of the Cl_2:NH_3-N ratios. Given that control of these ratios is critical to limiting the release of free ammonia into the distribution system, and therefore reducing nitrification potential, these adjustments are recommended.

The nitrite, nitrate, and ammonia data necessary to identify nitrification occurrence were largely unavailable. The limited nitrite and nitrate data collected by Fayetteville could not be included in this analysis due to suspect values, and ammonia concentrations were not measured in the distribution system. Although OWASA collected nitrogen data for a limited period during this study, the utility did not typically measure nitrite, nitrate, or ammonia concentrations in the distribution system. Raleigh also did not routinely measure nitrite, nitrate, or ammonia concentrations, and Durham measured only nitrate concentration. Although Greenville began to measure nitrite, nitrate, and ammonia concentrations in the summer of 2005, analytical discrepancies between measurements taken at the treatment plant and in the distribution system precluded comparison of POE and distribution system data. Thus, this study found that it is necessary for utilities to adjust their sampling practices to include routine measurement of these critical parameters in order to effectively monitor for nitrification.

This research also found that the frequency of data collection, both at the treatment plant and in the distribution system, may be critical to identifying nitrification occurrence. Analysis of nitrate data collected by OWASA demonstrates the need for frequent sampling at the treatment plant if parameter concentrations are highly variable at the POE. Although OWASA measured nitrate values on a weekly basis, the results were too variable to use POE averages to assess changes between the treatment plant and the distribution system. Perhaps more importantly, the data indicate that vulnerable distribution system sites may not be sampled at a frequency sufficient to identify episodes of nitrification. In Greenville, the two sites identified by this research as most vulnerable to nitrification were sampled only three and five times over the 3-year period of analysis. With such limited sampling, it is likely that nitrification occurrence could go undetected, regardless of the parameters measured. Therefore, it is important that utilities determine which sites hold the highest potential for nitrification and sample those sites regularly.

4.7.2 Water Treatment Plant

A summary of the treatment plant operating practices and finished-water quality characteristics evaluated in this study is provided in Table 4.11.

Table 4.11 Summary of results from treatment plant analyses

	UTILITY						
	Durham		Fayetteville		Greenville	OWASA	Raleigh
	Brown	Williams	Hoffer	Glenville			
POE Average[1] Total Cl_2 (mg/L as Cl_2)	3.1	2.9	3.4[3]	3.7[3]	3.7	3.2	3.6
Standard Deviation[1] (mg/L as Cl_2)	0.3	0.5	0.5	0.5	0.9	0.3	0.4
POE Average[1] Free NH_3 (mg/L as N)	0.42	0.41	0.25	0.27	0.20[5]	0.10[7]	0.64
Standard Deviation[1] (mg/L as N)	0.12	0.08	0.06	0.06	0.10	0.07	0.25
Average[1] Cl_2:NH_3-N Ratio (mg Cl_2 / mg N)	3.4:1[2]	3.1:1[2]	–[4]	4.0:1	3.6:1	5.5:1	3.8:1
Standard Deviation[1] (mg Cl_2 / mg N)	0.5:1	1.0:1	–	0.6:1	0.9:1	1.6:1	0.3:1
POE Average[1] pH	8.1	8.2	7.4	7.4	7.7	8.4	8.5
Standard Deviation[1]	0.3	0.3	0.1	0.1	0.1	0.2	0.4
POE Average[1] TOC (mg/L)	2.4	3.0	3.7	3.3	3.3	1.9	2.4
Standard Deviation[1] (mg/L)	0.3	0.6	1.2	1.1	0.6	0.4	0.2
Annual Switch to Free Cl_2	Yes	Yes	Yes	Yes	No[6]	Yes	Yes

[1] Averages and standard deviations calculated from daily values; [2] Approximated value; [3] Combined chlorine value; [4] Not calculated due to lack of sufficient data; [5] Calculated from total ammonia measurements; [6] Between 12/02 and 12/06, the switch to free chlorine was made only during April 2004; [7] Based upon 3 months of data only, during which time the average Cl_2:NH_3-N ratio was 7.7:1

The average total chlorine concentrations at the POE to the distribution system differed considerably among the five participating utilities. The average values ranged from 2.9 mg/L in Durham's system to 3.7 mg/L in the Fayetteville and Greenville systems. The variability in disinfectant residual at the POE to the Fayetteville, Greenville, and Raleigh distribution systems generally followed a seasonal trend, with peak concentrations typically occurring in the summer or fall. This seasonal trend is likely due to the accelerated chloramine decay and/or increased microbial activity associated with warmer water temperatures. While total chlorine concentrations at the POE were typically below 4.0 mg/L across all systems, residuals at Greenville were appreciably above 4.0 mg/L in recent months, thereby making the system vulnerable to violations of the MRDL established by Stage 1 of the D/DBP Rule.

The Cl_2:NH_3-N ratios used to form monochloramine also differed significantly across utilities, as did the free ammonia concentrations measured at the POE. While the average Cl_2:NH_3-N ratios used by Durham, Fayetteville, Greenville, and Raleigh were considerably below the 5:1 theoretically optimum value, the average ratio used by OWASA exceeded 5:1. The highest average concentration of free ammonia at the POE (0.64 mg/L) was found in Raleigh, where the average Cl_2:NH_3-N ratio was 3.8:1 mg Cl_2/mg N. (The Cl_2:NH_3-N ratio targeted by Raleigh was reported to be 3.0:1). Excess ammonia concentrations measured at Raleigh's POE were considerably higher than the values predicted based upon the ammonia dosages and free chlorine residuals at the PAA. Conversely, the average free ammonia concentration at Greenville's POE was unexpectedly low (0.20 mg/L) given the average Cl_2:NH_3-N ratio of only 3.6:1 mg Cl_2/mg N.

High average excess free ammonia concentrations (0.42 mg/L and 0.41 mg/L) were found in Durham, where the (approximated) Cl_2:NH_3-N ratios were the lowest at 3.4:1 and 3.1:1 mg Cl_2/mg N. The lowest average concentration of free ammonia at the POE (0.10 mg/L) was found at OWASA, where the average Cl_2:NH_3-N ratio was the highest at 5.5:1 mg Cl_2/mg N. Average excess free ammonia concentrations in Fayetteville were reasonably low (0.25 mg/L and 0.27 mg/L), and consistent with the relatively high average Cl_2:NH_3-N ratio at the Glenville Lake WTP (4.0:1 mg Cl_2/mg N). These findings demonstrate the correlation between higher Cl_2:NH_3-N ratios and lower concentrations of excess free ammonia, and thus support American Water Works Association Research Foundation (AwwaRF) recommendations to optimize Cl_2:NH_3-N ratios in order to minimize nitrification potential (see Section 2.2.4).

In view of AwwaRF recommendations and the high free ammonia concentrations at the POE in Durham and Raleigh, it may be advisable for these utilities to increase the Cl_2:NH_3-N ratios (or decrease the ammonia dosages) relative to current operations in order to limit the substrate available to nitrifying bacteria. This operational change may be particularly important for Raleigh, given that the average POE free ammonia concentration is over two times the average concentrations in Fayetteville, Greenville, and OWASA, and over 50% higher than the average concentration in Durham, and that the system has shown evidence of nitrification in the past. Conversely, the Cl_2:NH_3-N ratios used by OWASA appear exceedingly high. Despite monthly average ratios as high as 8.6:1, the system did not appear to experience disinfectant loss through the breakpoint reactions that would be expected from the utility's chloramine formation conditions. Relatively high Cl_2:NH_3-N ratios may therefore be appropriate for OWASA, though the reason for this is not apparent. Investigation into this matter may be appropriate to ensure that chlorine and ammonia dosages and chlorine residuals are being determined and recorded properly. Additionally, the utility may benefit from adjusting system operations to achieve more consistent Cl_2:NH_3-N ratios.

While Cl_2:NH_3-N ratios in Raleigh were reasonably consistent over time, the ratios in Durham, Fayetteville, Greenville, and OWASA were considerably variable. (Despite fairly stable Cl_2:NH_3-N ratios in Raleigh, however, excess free ammonia concentrations at the POE were highly variable.) These findings indicate that adjustments to the ammonia feed were not consistent with changes in free chlorine concentration at the PAA. Adjusting the ammonia feed as necessary to reflect changing disinfectant residual is optimal for preventing nitrification, as it stabilizes the release of free ammonia into the distribution system.

This study found that the reported ammonia dosages were typically approximated by the utilities using the daily amount of ammonia dosed (in pounds) and either daily filter effluent volume (Greenville) or daily raw water volume (Durham, OWASA, and Raleigh) instead of the actual volume of water to which ammonia was added. Filter effluent is a reasonable approximation of the ammoniated volume, though a portion of the filter effluent volume is commonly used for filter backwash and may not be ammoniated. Also, the assumption that filter effluent volume is equal to the ammoniated volume does not account for changing volume in clearwell storage. Raw water volume may differ appreciably from the volume of water to which ammonia is added, and therefore may not be an appropriate approximation for ammoniated water. Using raw water volumes to calculate ammonia dosages may result in a significant underestimate of the ammonia dosage, which in turn leads to an overestimate of the Cl_2:NH_3-N ratio. Because the Cl_2:NH_3-N ratios for Durham and OWASA were calculated using reported ammonia dosages based on raw water volumes, the ratios presented in this report may be somewhat higher than the true ratios. The availability of pumping records for Raleigh allowed for the calculation of more precise ammonia dosages.

The average pH values at the POE ranged from 7.4 in Fayetteville to 8.5 in Raleigh. Given the complex relationship between pH and nitrification evidenced by the wide range of pH values at which nitrification has been found to occur, it is not possible to identify an optimum pH condition. More importantly, finished-water pH tends to be driven by requirements for corrosion control. The average TOC concentrations at the POE ranged from 1.9 mg/L at OWASA to 3.7 mg/L in Fayetteville. The variability in finished-water TOC values in Fayetteville is significant, with standard deviations at the Hoffer WTP and the Glenville Lake WTP of 1.2 mg/L and 1.1 mg/L, respectively. As described in Section 2.2.4, minimizing the introduction of organic material into the distribution system acts to reduce nitrification potential by limiting chloramine demand and improving the biological stability of the water. Maximizing the removal of organic material in the treatment plant has the added benefit of minimizing the formation of chlorine-related DBPs during periods of free chlorination.

The practice of switching from chloramines to free chlorine for a period of one month annually (typically in March) was observed by all utilities except Greenville; Greenville switched to free chlorine only once (April 2004) during the 3-year period of analysis. The reason for this is not known. Although the temporary change in secondary disinfectant has been found to be a more effective control measure than a preventive measure, the practice is widely employed and may help to delay or prevent nitrification occurrence.

4.7.3 Distribution System

Disinfectant residuals sufficiently low to favor nitrifying activity were detected in all distribution systems. Total chlorine concentrations below 1.0 mg/L were found in all systems, though the most recurring low residuals were found in Raleigh. (Relatively recent structural and operational changes by the utility, however, have improved disinfectant stability to some extent.) This finding is consistent with the high HRTs found in large distribution systems such as Raleigh's, as well as the utility's high percentage of iron piping in its distribution system. Further, the high concentration of ammonia introduced from Raleigh's treatment plant may have contributed to these low residuals by favoring nitrification, though the available data did not allow for an assessment of nitrification.

In Durham, where nitrate data were routinely collected at the POE and in the distribution system, the data provided suggest that nitrification may have occurred at distribution site E30 in October and November 2004. This potential nitrification episode was evidenced by a prolonged period of low disinfectant residual and corresponding increases in nitrate concentration. Total chlorine concentrations reached values as low as 0.40 mg/L during this period, and nitrate concentration increased as much as 0.5 mg/L relative to the POE. This potential nitrification occurrence was also marked by increased HPC and high water temperature (24°C).

In the absence of critical nitrogen data, the analysis of the HPC, pH, and DO data offered little insight into the identification of nitrification episodes. The HPC data provided by Greenville, OWASA, and Raleigh generally failed to support a significant inverse relationship between HPC and low disinfectant residual. Similarly, analysis of pH data provided by these same three utilities indicated poor correlation between decreases in pH values and low disinfectant residual. Analysis of DO data provided by Greenville found that DO concentrations at the POE were too variable to allow for detection of the relatively small decreases in DO associated with nitrification.

CHAPTER 5 – CONCLUSIONS & RECOMMENDATIONS

Historical treatment plant and distribution system data from each of the five chloraminating members of the North Carolina Urban Water Consortium were analyzed to assess nitrification potential and occurrence. Limited sampling of the occurrence of NDMA was also done for two of the systems. The results of this study led to the conclusions and recommendations listed below.

5.1 CONCLUSIONS

- The data required to calculate the Cl_2:NH_3-N ratios at the Hoffer WTP in Fayetteville were not routinely measured by the utility. The data necessary to calculate the Cl_2:NH_3-N ratios at each of the two PAAs in Raleigh's treatment plant were also not measured, and only the plant average ratios could be determined. The information needed to calculate the ratios at Durham's Brown and Williams WTPs were not provided (though all necessary parameters were routinely measured); thus the Cl_2:NH_3-N ratios were approximated from available data.

- The nitrite, nitrate, and ammonia measurements critical to the detection of nitrification were largely unavailable at all utilities. The data necessary to assess change in these parameters were not routinely collected at the treatment plant or in the distribution system, or both. In some cases (Fayetteville and Greenville), the appropriate parameters were routinely measured, but analytical discrepancies precluded the use of these data. In another case (Raleigh), the ammonia concentrations measured at the POE appeared unrealistically high. These findings suggest that analytical methods/procedures used by the utilities need to be evaluated to improve data reliability.

- The chlorine-to-ammonia ratios used to form monochloramine differed considerably across the five utilities. While Durham, Fayetteville, Greenville, and Raleigh generally used Cl_2:NH_3-N weight ratios below the 5:1 theoretically optimum value, OWASA's Cl_2:NH_3-N ratios were generally well in excess of 5:1. (The need for, and the underlying reason behind, the exceedingly high ratios observed at OWASA is not apparent.) While the ratios used by Raleigh were reasonably stable over the period of analysis, the ratios at Durham, Fayetteville, Greenville, and OWASA were highly variable.

- The free ammonia concentrations measured at the POE also differed considerably across, and in some cases within, utilities. The highest and most variable concentrations of excess free ammonia were found in Raleigh and Durham. The values measured in Raleigh greatly exceeded expected values, making it particularly vulnerable to nitrification occurrence. POE free ammonia concentrations were lowest at OWASA, and concentrations were comparable between Fayetteville and OWASA.

- The data generally supported the theoretical relationship between decreasing Cl_2:NH_3-N ratios and increasing excess free ammonia.

- Disinfectant residuals sufficiently low to favor nitrifying activity were detected in all distribution systems. Total chlorine concentrations below 1.0 mg/L were found in all systems, though the most recurring low residuals were detected in Raleigh.

- Evidence of nitrification was detected at distribution site E30 in Durham in October and November 2004. This apparent nitrification episode was marked by a prolonged period of low disinfectant residual, increased nitrate concentration, increased HPC, and warm water temperatures. (Although high excess ammonia concentrations at the POE and low disinfectant residuals in the distribution system suggest that Raleigh's nitrification potential was high, data were not available to assess nitrification occurrence in this system.)

- Vulnerable distribution system sites in Greenville were found to have been sampled very few times over the period of analysis. Certain vulnerable sites in Fayetteville and Raleigh were also sampled relatively infrequently. Without more frequent sampling at such locations, nitrification episodes may go undetected.

- Where certain parameters were highly variable at the POE (Greenville and OWASA), sampling frequency was found to be insufficient to allow for comparison between the POE and distribution system measurements.

- Concentrations of total and combined chlorine at the POE to the distribution system differed considerably across, and in some cases within, utilities. While POE disinfectant residuals were typically below the MRDL of 4.0 mg/L in all systems, recent POE total chlorine concentrations at Greenville were considerably higher than 4.0 mg/L.

- Durham, OWASA, and Raleigh reported ammonia dosages approximated using pounds of ammonia dosed and the daily raw water volume in lieu of the actual volume of water to which ammonia was added. Therefore, the true ammonia dosages should be higher than those reported by the utilities, and this approximation leads to an overestimate of the Cl_2:NH_3-N ratios.

- Decreases in pH between the treatment plant and the distribution system, as well as increases in HPC within the distribution system, were found to be poorly correlated with low disinfectant residuals.

- Limited sampling of sites in the Raleigh and Durham distribution systems associated with low chloramine residuals and exhibiting historical evidence of nitrification showed NDMA to be present at concentrations below 10 ng/L, the Notification Level for this emerging DBP in California.

5.2 RECOMMENDATIONS

- Fayetteville should consider measuring free chlorine residual immediately prior to ammonia addition at the Hoffer WTP to allow for the calculation of the Cl_2:NH_3-N ratios. Raleigh should consider measuring the ammonia dosages at each of the two PAAs to allow for the calculation of the Cl_2:NH_3-N ratios at each location, instead of plant average ratios.

- All utilities should consider adjusting existing sampling plans to include routine (e.g. weekly) measurements of nitrite, nitrate, and ammonia, both at the POE and in the distribution system, particularly at sites with low disinfectant residuals and/or high water ages. (Where these parameters are routinely measured and analytical discrepancies were identified, these discrepancies should be resolved.) Also, where POE values are highly variable, more frequent sampling at the plant may be appropriate.

- Fayetteville, Greenville and, in particular, Durham and Raleigh should consider upward adjustments to Cl_2:NH_3-N ratios in order to minimize the concentrations of free ammonia entering the distribution system and thereby reducing nitrification potential.

- Greenville should consider modifying treatment and operating conditions to reduce the concentration of total chlorine at the POE to the distribution system, as current operations make the utility vulnerable to violations of the MRDL of 4.0 mg/L established by Stage 1 of the D/DBP Rule.

- Durham, OWASA, and Raleigh should consider calculating ammonia dosages using the actual volume of water to which ammonia is added, or a close approximation such as filter effluent volume, in lieu of raw water volume. This will allow for more accurate calculations of ammonia dosages and the corresponding Cl_2:NH_3-N ratios.

- OWASA should verify that its Cl_2:NH_3-N ratios are indeed greater than 5:1 by checking the calibration of meters that monitor the chlorine and ammonia feeds, and verify that the data provided for this study are correct.

REFERENCES

AWWA and Economic and Engineering Services (EES), Inc. (2003). Nitrification, http://www.epa.gov/safewater/tcr/pdf/nitrification.pdf. Accessed 6-23-06.

Besner, M., V. Gauthier, P. Servais, and A. Camper. (2002). Explaining the occurrence of coliforms in distribution systems. *Jour. AWWA*, 94(8):95-109.

Bone, C. C., G. W. Harrington, P. S. Oldenburg, and D. R. Noguera. (1999). Ammonia release from chloramine decay: implications for the prevention of nitrification episodes. In Proceedings of the Annual AWWA Conference. Denver, CO.

Camp Dresser & Mckee (CDM). (2006). Phase 2 Coliform Compliance Study, Final Report.

Camper, A. K., W. L. Jones, and J. T. Hayes. (1996). Effect of growth conditions and substratum composition on the persistence of coliforms in mixed-population biofilms. *Applied and Environmental Microbiology*, 62(11):4014-4018.

Camper, A. K., K. Brastrup, A. Sandvig, J. Clement, C. Spencer, and A. J. Capuzzi. (2003). Effect of distribution system materials on bacterial regrowth. *Jour. AWWA*, 95(7):107-120.

Chadwick, J. (2006). Greenville Utilities Commission. Personal communication.

Charrois, J. W., & S. E. Hrudey. (2007). Breakpoint chlorination and free-chlorine contact time: Implications for drinking water N-nitrosodimethylamine concentrations. *Water Res* 41(3):674-682.

Chen, X., and P. S. Stewart. (1996). Chlorine penetration into artificial biofilm is limited by a reaction-diffusion interaction. *Environmental Science and Technology*, 30(6):2078-2083.

Choi, J. and R. L. Valentine. (2002). Formation of *N*-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product. *Water Research*, 36(4):817-824.

Cunliffe, D. A. (1991). Bacterial nitrification in chloraminated water supplies. *Applied and Environmental Microbiology*, 57(11):3399-3402.

Diehl, A. C., E. Speitel Jr., J. M. Symons, S. W. Krasner, S. J. Hwang, S. E. Barrett. (2000). DBP formation during chloramination. *Jour. AWWA*, 92(6):76-90.

DiGiano, F. A., D. E. Francisco, W. Zhang, and L. Todd. (2000). *Bacterial Regrowth in Drinking Water Distribution Systems: A Comparison of Durham and Raleigh,* Report No. 326. Water Resources Research Institute of UNC. Raleigh, NC.

DiGiano, F. A., W. Zhang, A. Travaglia, D. E. Francisco, and M. Wood. (2002). *Occurrence of Bacterial Regrowth and Nitrification in the Raleigh Distribution System and Development of an EPANET Model for Future Assessments,* Report No. 338. Water Resources Research Institute of UNC. Raleigh, NC.

Durham Environmental Resources Department. http://www.ci.durham.nc.us. Accessed 7/2/06.

Edwards, M., B. Marshall, Y. Zhang, and Y. Lee. (2004). Unintended consequences of chloramination hit home. In Proceedings of Water Environment Federation Conference.

Fayetteville Public Works Commission. http://www.faypwc.com. Accessed 7/2/06.

Ferguson, B. A. (2005). Impact of temporary switches from chloramines to free chlorine on water quality in distribution systems. Master's Thesis, University of North Carolina at Chapel Hill.

Forkner, L. (2006). Raleigh Public Utilities Department. Personal communication.

Greenville Utilities Commission. http://www.guc.com. Accessed 7/2/06.

Griebe, T., C. Chen, R. Srinivasan, and P. S. Stewart. (1993). Analysis of biofilm disinfection by monochloramine and free chlorine. *Biofouling and Biocorrosion in Industrial Water Systems.* (Geesey et al., editors.) Chapter 9, pp. 151-161. Lewis Publishing, Inc. Boca Raton, FL.

Hao, O. J., C. M. Chien, and R. L. Valentine. (1994). Kinetics of monochloramine reactions with nitrite. *Jour. of Environmental Engineering – ASCE*, 120(4):859-874.

~~Han, N. J. (2005). Estimated compliance with the proposed Stage 2 Disinfection By-Products Rule for eleven water utilities in North Carolina. Master's Thesis, University of North Carolina at Chapel Hill.~~

Harrington, G. W., D. R. Noguera, A. I. Kandou, and D. J. Vanhoven. (2002). Pilot-scale evaluation of nitrification control strategies. *Jour. AWWA*, 94(11):78-89.

Harrington, G. W., D. R. Noguera, C. C. Bone, A. I. Kandou, P. S. Oldenburg, J. M. Regan, and D. Van Hoven. (2003). *Ammonia from Chloramine Decay: Effects on Distribution System Nitrification.* AWWA Research Foundation and AWWA. Denver, CO.

Hoyle, Clifton. (2006). Raleigh Public Utilities Department. Personal communication.

Hynes, R. K. and R. Knowles. (1983). Inhibition of chemoautotrophic nitrification by sodium chlorate and sodium chlorite: a reexamination. *Applied and Environmental Microbiology*, 45(4):1178-1182.

Kirmeyer, G., K. Martel, G. Thompson, and L. Radder. (2004). *Optimizing Chloramine Treatment, 2nd Edition*. AWWA Research Foundation and AWWA. Denver, CO.

Koudjonou, B. K., et al. (1998). Chlorine versus chloramine: impact on the composition of a drinking water biofilm. CD-ROM Paper 3C.2. In Proceedings of AWWA Water Quality Technology Conference. Denver, CO.

Krasner, S. W., J. J. McGuire, J. G. Jacangelo, N. L. Patania, K. M. Reagan, and E. M. Aieta. (1989). The occurrence of disinfection by-products in U.S. drinking water. *Jour. AWWA*, 81(8):41-53.

LeChevallier, M. W., T. M. Babcock, and R. G. Lee. (1987). Examination and characterization of distribution system biofilms. *Applied and Environmental Microbiology*, 53(12):2714-2724.

LeChevallier, M. W., C. D. Cawthon, and R. G. Lee. (1988). 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. *Jour. AWWA*, 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. *Jour. AWWA*, 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.

Lieu, N. I., R. L. Wolfe, and E. G. Means. (1993). Optimizing chloramine disinfection for the control of nitrification. *Jour. AWWA*, 85(2):84-90.

Margerum, D. W., L. M. Schurter, J. Hobson, and E. E. Moore. (1994). Water chlorination chemistry: nonmetal redox kinetics of chloramine and nitrite ion. *Environmental Science and Technology*, 28(2):331-337.

McGuire, M. J., N. I. Lieu, and M. S. Pearthree. (1999). Using chlorite ion to control nitrification. *Jour. AWWA*, 91(10):52-61

McGuire, M. J., M. S. Pearthree, N. K. Blute, K. F. Arnold, T. Hoogerwerf. (2006). Nitrification control by chlorite ion at pilot scale. *Jour. AWWA*, 98(1):95-105.

Mitch, W. A., & D. L. Sedlak. (2002). Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environ Sci Technol* 36:588-595.

Moffat, E. (2006). Nitrosamines Sampling and Analytical Methods. Personal communication.

~~Monschein, R. (2006). Orange Water and Sewer Authority. Personal communication.~~

Neden, D. G., R. J. Jones, J. R. Smith, G. J. Kirmeyer, and G. W. Foust. (1992). Comparing chlorination and chloramination for controlling bacterial regrowth. *Jour. AWWA*, 84(7):80-88.

Norton, C. D. and M. W. LeChevallier. (1997). Chloramination: its effects on distribution system water quality. *Jour. AWWA*, 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. *Jour. AWWA*, 88(7):86-98.

Ollos, P. J., P. M. Huck, and R. M. Slawson. (2003). Factors affecting biofilm accumulation in model distribution systems. *Jour. AWWA*, 95(1):87-97.

Orange Water and Sewer Authority (OWASA). http://www.owasa.org. Accessed 7/2/06.

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.

Pintar, K. D. M., W. B. Anderson, R. M. Slawson, E. F. Smith, and P. M. Huck. (2005). Assessment of a distribution system nitrification critical threshold concept. *Jour. AWWA*, 97(7):116-129.

Raleigh Public Utilities Department. http://www.raleigh-nc.org. Accessed 7/2/06.

Regan, J. M., G. W. Harrington, and D. R. Noguera. (2002). Ammonia- and nitrite-oxidizing bacterial communities in a pilot-scale chloraminated drinking water distribution system. *Applied and Environmental Microbiology*, 68(1):73-81.

Regan, J. M., G. W. Harrington, H. 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.

Reiber, S. (1993). Investigating the effects of chloramine on elastomer degradation. *Jour. AWWA*, 85(8):101-111.

Seidel, C. (2005). Have utilities switched to chloramines? Results from the AWWA disinfection practices survey. AWWA Annual Conference. San Francisco, CA.

Skadsen, J. (1993). Nitrification in a distribution system. *Jour. AWWA*, 85(7):95-103.

Skadsen, J. (2002). Effectiveness of high pH in controlling nitrification. *Jour. AWWA*, 94(7):73-83.

Smith, C. (2006). Fayetteville Public Works Commission. Personal communication.

Snoeyink, V. L., and D. Jenkins. (1980). *Water Chemistry*. John Wiley & Sons. New York.

Song, D. J., A. Sheikholeslami, L. L. Hoover, K. A. Turner, H. H. Lai, and A. Wilczak. (1999). Improvement of chloramine stability through pH control, TOC reduction and blending at EBMUD. In Proceedings of AWWA Annual Conference. Chicago, IL.

Sullivan, L. and McGuire Environmental Consultants. (2005). An innovative technique for controlling nitrification in chloraminating systems. AWWA Annual Conference. San Francisco, CA.

USEPA. (1993). *USEPA Manual: Nitrogen Control.* EPA/625/R-93/010. United States Environmental Protection Agency. Washington, DC.

USEPA. (1996). Information Collection Rule. *Federal Register,* 61(94):24354.

USEPA. (2002) N-Nirosodimethylamine (CASRN 62-75-9). 2007**:** 8.

Valentine, R. L. and C. T. Jafvert. (1988). General acid catalysis of monochloramine disproportionation. *Environmental Science and Technology*, 22(6):691-696.

Valentine, R. L., K. Ozekin, and P. J. Vikesland. (1998). *Chloramine Decomposition in Distribution System and Model Waters.* AWWA Research Foundation and AWWA. Denver, CO.

Valentine, R. L., P. J. Vikesland, B. D., Angermand, S. A. Hackett, M. Shoup, and S. Slattenow. (2000). *The Role of the Pipe-Water Interface in DBP Formation and Disinfectant Loss.* AWWA Research Foundation and AWWA. Denver, CO.

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 and Technology*, 32(10):1409-1416.

Vikesland, P. J. and R. L. Valentine. (2000). Reaction pathways involved in the reduction of monochloramine by ferrous iron. *Environmental Science and Technology*, 34(1):83-90.

Vikesland, P. J., K. Ozekin, and R. L. Valentine. (2001). Monochloramine decay in model and distribution system waters. *Water Research*, 35(7):1766-1776.

Watson, S. W., F. W. Valos, and J. B. Waterbury. (1981). The Family Nitrobacteraceae. *The Prokaryotes.* (M. P. Starr et al., editors.) Springer Verlag. Berlin, Germany.

Watson, S. W., E. E. Bock, H. Harms, H. P. Koops, and A. B. Hooper. (1989). Nitrifying bacteria. *Bergey's Manual of Systematic Bacteriology*, Vol. 3. (J. T. Saley et al., editors.) Williams & Wilkins. Baltimore, Md.

Westbrook, J. A. (2006). Determination of chloramine decay rates at pipe surfaces and in bulk water in a simulated distribution system environment. Master's Thesis, University of North Carolina at Chapel Hill.

White, C. G. (1986). *Handbook of Chlorination and Alternative Disinfectants, 2nd Edition.* Van Nostrand Reinhold Co. New York.

White, C. G. (1999). *Handbook of Chlorination and Alternative Disinfectants, 4th Edition.* John Wiley & Sons, Inc. New York.

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. *Jour. AWWA*, 88(7):74-85.

Wilczak, A., L. L. Hoover, and H. H. Lai. (2003). Effects of treatment changes on chloramine demand and decay. *Jour. AWWA*, 95(7):94-106.

Wolfe, R. L., N. R. Ward, and B. H. Olson. (1985). Interference in the bactericidal properties of inorganic chloramines by organic nitrogen compounds. *Environmental Science and Technology*, 19(12):1192-1195.

Wolfe, R. L., E. G. Means, M. K. Davis, and S. E. Barrett. (1988). Biological nitrification in covered reservoirs containing chloraminated water. *Jour. AWWA*, 80(9):109-114.

Wolfe, R. L., N. I. Lieu, G. Izaguirre, and E. G. Means. (1990). Ammonia-oxidizing bacteria in a chloraminated distribution system: seasonal occurrence, distribution, and disinfection resistance. *Applied and Environmental Microbiology*, 56(2):451-462.

Wood, P. M. (1986). Nitrification as a bacterial energy source. *Nitrification*. IRL Press. Oxford, UK.

Woolschlager, J., B. E. Rittman, P. Piriou, and B. Schwartz. (2001a). Developing an effective strategy to control nitrifier growth using the comprehensive disinfection and water quality model. In Proceedings of World Water and Environmental Resources Congress, ASCE. Renton, VA.

Woolschlager, J., B. Rittmann, P. Piriou, L. Kiene, and B. Schwartz. (2001b). Using a comprehensive model to identify the major mechanisms of chloramine decay in distribution systems. *Water Science and Technology: Water Supply*, 1(4):103-110.

APPENDIX

Table A.1: Raw-water total ammonia removal through pretreatment (Greenville)

DATE	LOCATION	Total NH_3 (mg/L as N)
5/23/2006	Raw Water	0.33
	Prior to PAA	0.27
5/25/2006	Raw Water	0.27
	Prior to PAA	0.21
5/30/2006	Raw Water	0.38
	Prior to PAA	0.16
6/6/2006	Raw Water	0.38
	Prior to PAA	0.29
6/7/2006	Raw Water	0.30
	Prior to PAA	0.18
6/8/2006	Raw Water	0.30
	Prior to PAA	0.21
6/9/2006	Raw Water	0.32
	Prior to PAA	0.24
6/12/2006	Raw Water	0.24
	Prior to PAA	0.07
6/13/2006	Raw Water	0.25
	Prior to PAA	0.10
6/14/2006	Raw Water	0.44
	Prior to PAA	0.29
6/15/2006	Raw Water	0.32
	Prior to PAA	0.25
6/16/2006	Raw Water	0.41
	Prior to PAA	0.22

Table A.2: Comparison of duplicate sampling results from Water Treatment Plant and Wastewater Treatment Plant laboratories (Greenville)

	Total NH_3 (mg/L as N)			$NO_2^- + NO_3^-$ (mg/L as N)		
SAMPLE	WTP	WWTP	Discrepancy	WTP	WWTP	Discrepancy
1	0.67	0.75	0.09	0.70	0.42	-0.28
2	0.60	0.83	0.23	0.80	0.41	-0.39
3	0.61	0.64	0.03	0.80	0.44	-0.36
4	0.63	0.62	-0.01	0.90	0.44	-0.46
5	0.66	0.64	-0.02	0.70	0.42	-0.28
6	0.62	0.65	0.04	0.70	0.43	-0.27
7	0.64	0.59	-0.05	0.90	0.44	-0.46
8	0.59	0.70	0.11	0.60	0.45	-0.15
9	0.66	0.62	-0.04	0.60	0.32	-0.28
10	0.69	0.83	0.14	0.80	0.33	-0.47
11	0.73	0.57	-0.16	0.90	0.26	-0.64
12	0.72	0.52	-0.20	0.90	0.33	-0.57
13	0.69	0.56	-0.13	0.70	0.41	-0.29
14	0.72	0.69	-0.03	0.80	0.42	-0.38
15	0.65	0.58	-0.07	0.70	0.44	-0.26

Table A.3: Raw-water total and free ammonia removal through the pretreatment process (OWASA)

		PARAMETER	
DATE	LOCATION	Total NH_3 (mg/L as N)	Free NH_3 (mg/L as N)
4/18/2006	Raw Water	<0.10	<0.02
	Prior to PAA	<0.10	<0.02
5/2/2006	Raw Water	<0.10	0.03
	Prior to PAA	<0.10	<0.02
5/10/2006	Raw Water	<0.10	0.08
	Prior to PAA	<0.10	<0.02
5/16/2006	Raw Water	<0.10	<0.02
	Prior to PAA	<0.10	<0.02
5/24/2006	Raw Water	<0.10	0.03
	Prior to PAA	<0.10	<0.02
5/31/2006	Raw water (Cane Creek)	<0.10	<0.02
	Raw water (University Lake)	1.37	0.58
	Prior to PAA	<0.10	<0.02
6/21/2006	Raw water (Cane Creek)	<0.10	0.03
	Raw water (University Lake)	0.326	0.23
	Prior to PAA	<0.10	<0.02

Table A.4: An illustration of nitrification in a satellite distribution system (Raleigh)

Site[1] #	Total Chlorine (mg/L)	Ammonia (mg/L)	Nitrite (mg/L)	Nitrate (mg/L)
1 [2]	2.80	0.63	< 0.02	0.06
2	0.20	0.09	0.58	0.37
3	0.30	0.11	0.28	0.62
4	0.70	0.08	< 0.02	0.85
5	0.20	0.11	0.12	0.92

[1] Site #s are listed in order of increasing residence time;

[2] Inlet to this satellite system