Effectiveness of Periodic Breakpoint Chlorination on Distribution System Nitrification Control for Pinellas County Utilities

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Many water utilities have switched from free chlorine to chloramines for secondary disinfection, primarily to comply with the disinfection byproduct regulations. Based on a survey conducted in 2005, 29 percent of the investigated utilities in the United States were using chloramines as secondary disinfectants (Seidel et al., 2005). Chloramination is a practical and highly effective disinfection byproduct control method; however, the application of chloramines in drinking water has caused concerns and water quality issues, including nitrification in the distribution system, distribution pipe corrosion, and formation of highly toxic nitrogenous byproducts (e.g., N-Nitrosodimethylamine) and iodinated disinfection byproducts (Singer, 2006).

Distribution system nitrification is a common problem for water utilities that use chloramines for secondary disinfection. Nitrification is a microbial process by which free ammonia released through chloramines decay is sequentially oxidized to nitrite and nitrate. Nitrification in the distribution system can have serious adverse effects on water quality, such as loss of chlorine residuals, release of free ammonia, production of nitrite/nitrate, decreased pH and dissolved oxygen, and increased microbiological activity (Wilczak et al., 1996). Typical nitrification control measures include:

- Increase entry-point and distribution total residual chlorine levels.
- Reduce free ammonia levels by using high Cl_2: NH_3 ratios.
- Reduce water age through hydraulics improvements and storage facility management.
- Flush distribution pipes and replace aged pipes.
- Perform periodic free chlorine maintenance.

Periodic switching from chloramines to free chlorine has been used by utilities to control distribution system nitrification. This process is also referred to as breakpoint chlorination or free chlorine maintenance. During the breakpoint chlorination process, sufficient free chlorine is added to drinking water to oxidize free ammonia and pre-existing chloramines to nitrogen gas so that appropriate free chlorine residuals are maintained in the distribution system. Free chlorine can effectively inactivate bacteria responsible for nitrification in the system and inhibit the occurrence of nitrification.

Annual breakpoint chlorination of the entire system has been used by some utilities for nitrification control. Breakpoint chlorination can also be used in affected sections or water storage tanks in the distribution system. Evidence of nitrification, such as increased nitrite levels, often triggers a temporary switch to free chlorine.

The effectiveness of breakpoint chlorination on nitrification control is affected by many factors, including temperature, water age, distribution system pipe conditions, and water quality. The primary objective of this research is to evaluate the effectiveness of switching to free chlorine for nitrification control in the distribution system of Pinellas County Utilities. The effect of breakpoint chlorination on water quality is also evaluated.

Table 1. Summary of Historical Free Chlorine Maintenance Events (2004–2010)

Year	Start	End	Duration (Days)
2004	October 25	November 14	21
2005	December 5	January 9, 2006	35
2006	September 18	October 23	35
2007	September 10	October 8	28
2008	August 25	September 29	35
2009	July 30	September 7	39
2010	August 23	October 4	41

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Pinellas County Utilities Water System

The utility provides drinking water to a population of approximately 700,000 along Florida's central-west coast. The County's water system has over 110,000 retail service customer connections and 24 wholesale customer connections. The distribution system of the utility includes five pump stations and approximately 2,000 miles of piping.

All water supplied by the utility is derived from sources owned and operated by Tampa Bay Water, the region's wholesale provider. The County's source water treatment system consists of the S.K. Keller Water Treatment Plant and the Regional Treatment Facility. The treatment plant treats groundwater from the Eldridge Wilde Wellfield; the treatment facility treats the regional water.

The treatment plant uses free chlorine for primary disinfection. Ammonia is added to the chlorinated water after the required contact time to form chloramines before

distribution. Tampa Bay Water uses ozone as a primary disinfectant and chloramines as the secondary disinfectant for the regional water. Under normal operating conditions, the treatment facility adds small amounts of free chlorine to combine the free ammonia in the regional water. Other chemicals added at the treatment plant and treatment facility include fluorosilicic acid, blended phosphate, and caustic soda.

The utility has observed nitrification episodes in the distribution system since the system was converted to chloramines for secondary disinfection in 2002 (Powell, 2004). The County's total water supply has decreased by 20 percent over the past 10 years. This decreased water use in this chloraminated system has contributed to persistent nitrification issues and low disinfectant residuals that are being remediated through increased water flushing and periodic free chlorine maintenance. Table 1 summarizes the historical free chlorine maintenance of the utility from 2004 to 2010. Free chlorine residuals at entry points were typically maintained at 3.5 to 4.5 mg/L during these free chlorine maintenance events.

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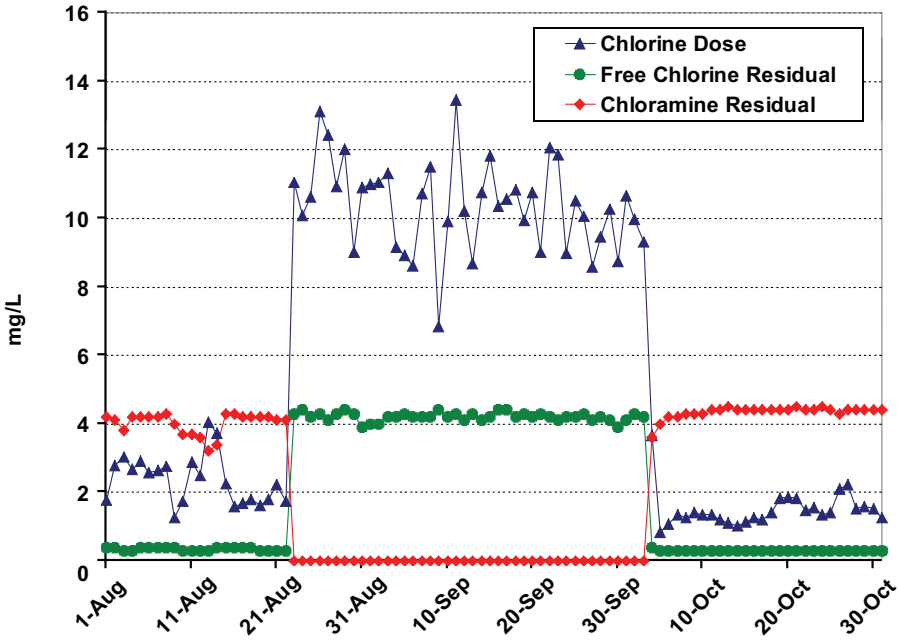

Figure 1. Regional Treatment Facility Free Chlorine Maintenance (2010)

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Breakpoint Chlorination Chemistry

The utility's water system is unique in that part of the system is a consecutive system receiving chloraminated regional water. During the free chlorine maintenance, the treatment facility needs to add adequate free chlorine to oxidize the chloramines in the regional water and maintain a target-free chlorine residual of 4 mg/L. Unlike the treatment facility, the treatment plant simply stops the ammonia feed system and maintains a free chlorine residual target of 3.5 to 4.0 mg/L during free chlorine maintenance.

Figure 1 presents the chlorine dose, free chlorine residual, and chloramines residual of the treatment facility from August to October 2010. The free chlorine dose at the treatment facility varied from 6.9 to 13.5 mg/L, with an average of 10.2 mg/L during the free chlorine maintenance in September 2010. The finished water free chlorine residual varied from 3.9 to 4.4 mg/L, with an average of 4.2 mg/L. The regional water typically has chloramines residual of 3.5 to 4.5 mg/L, with an average of 4.0 mg/L. Based on the utility's experience, an average free chlorine dose of 10 mg/L is needed to oxidize an average chloramines residual of 4 mg/L to maintain a free chlorine residual of 4 mg/L in the regional water. The required chlorine-to-chloramine ratio at the treatment facility for breakpoint chlorination is approximately 2.5.

Figure 2 presents a theoretical breakpoint chlorination curve. The distribution of mono-, di-, and trichloramines primarily depends on chlorine-to-ammonia ratio and pH. Monochloramine is predominant at low Cl_2:NH_3-N ratios (e.g., < 5 mg Cl_2/mg N). Free chlorine residual appears when chlorine-to-ammonia ratio exceeds a certain point (e.g., Cl_2:NH_3-N >7.6).

Theoretically, a free chlorine dose of 2.0 mg/L is needed to achieve the breakpoint (Cl_2:NH_3-N = 7.6) for water with a monochloramine residual of 4 mg/L. A minimum 6 mg/L free chlorine dose is required to oxidize 4 mg/L monochloramine and maintain a free chlorine residual of 4 mg/L. Additional 4 mg/L free chlorine dose (a total of 10 mg/L) is needed at the treatment facility to oxidize chloramines and meet the chlorine demands from organic and inorganic compounds in water.

Equations (1) through (9) summarize the major reactions that may occur during the breakpoint chlorination. Mono-, di-, and trichloramines are some of the intermediate products of the process. The reactions of the breakpoint chlorination are generally fast, according to the kinetic data (Huang, 2008). Reaction (5) is believed to be the rate-limiting step of the entire mechanism. Nitroxyl radical (NOH) is produced in this step and is the key mechanism for chloramines loss during breakpoint chlorination. The end products of breakpoint chlorination are primarily nitrogen gas (N_2) and secondarily nitrate (NO_3^-).

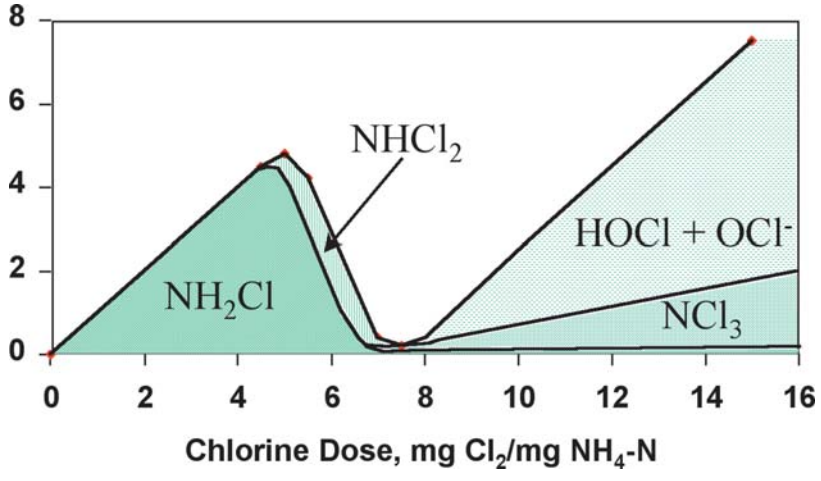
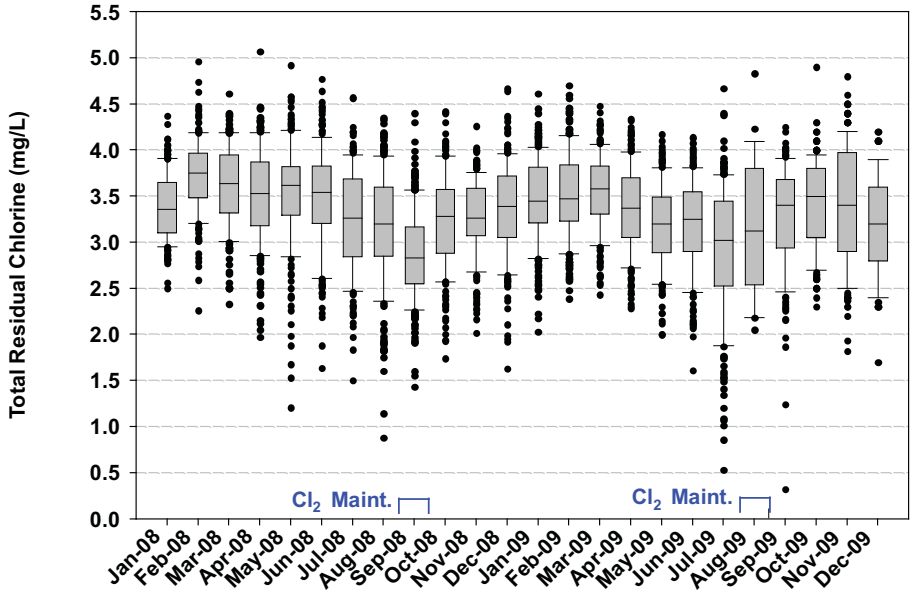


Figure 2. Theoretical Breakpoint Chlorination Curve



Box: 25 Percent, 50 percent, and 75 percent
Whiskers (error bars): 10 percent and 90 percent
Circles: Outliers

Figure 3. Distribution System Routine Site Monthly Average Total Chlorine (2008–2009)

(1) $NH_3 + HOCl \rightarrow NH_2Cl = H_2O$
(k =2.04x10^{9}exp(-1887/T)M^{-1}s^{-1})
(2) $NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$
(k=3.0x10^{5}exp(-2010/T) M^{-1}s^{-1})
(3) $NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$
(k=3.28x10^9 M^{-2}s^{-1})
(4) $NCl_3 + H_2O \rightarrow NHCl_2 + HOCl$
(k=65 M^{-2}s^{-1})
(5) $NHCl_2 + H_2O \rightarrow NOH + 2HCl$
(k=1.67x10^2 M^{-1}s^{-1})
(6) $NOH + NHCl_2 \rightarrow HOCl + N_2 + HCl$
(k=2.77x10^4 M^{-1}s^{-1})
(7) $NOH + NH_2Cl \rightarrow N_2 + HCl + H_2O$
(k=8.3x10^3 M^{-1}s^{-1})

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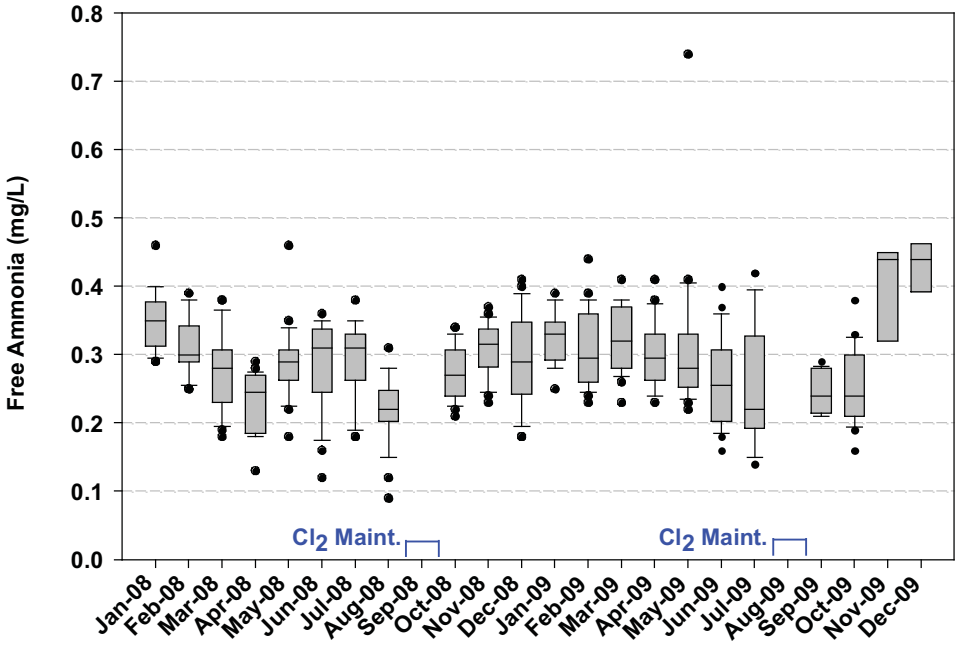

Figure 4. Distribution System Routine Site Monthly Average Free Ammonia (2008–2009)

Box: 25 Percent, 50 percent, and 75 percent
Whiskers (error bars): 10 percent and 90 percent
Circles: Outliers

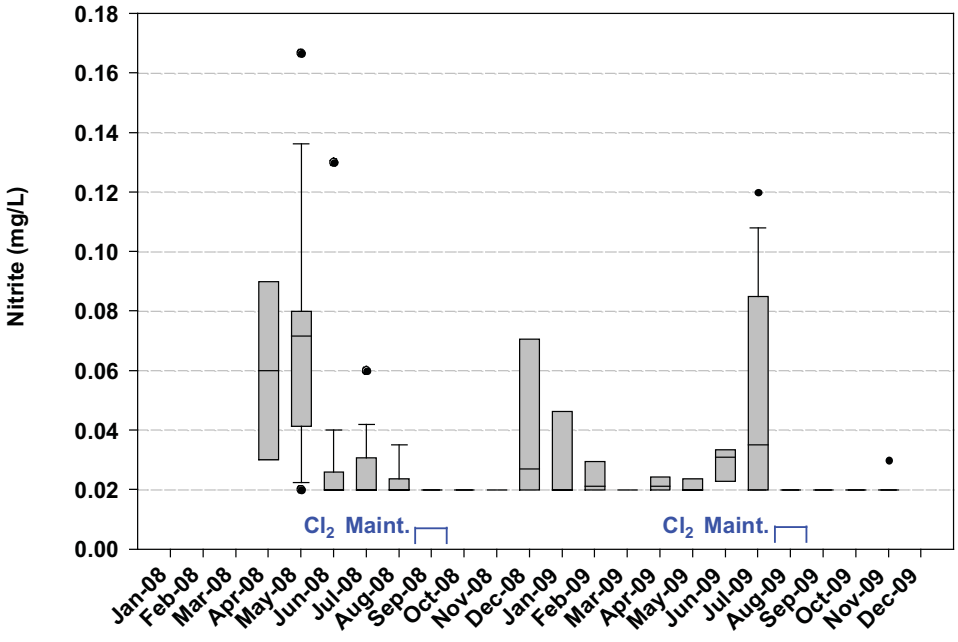

Figure 5. Distribution System Routine Site Monthly Average Nitrite (2008–2009)

Box: 25 Percent, 50 percent, and 75 percent
Whiskers (error bars): 10 percent and 90 percent
Circles: Outliers

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(8) $NHCl_2 + NCl_3 + H_2O \rightarrow HOCl + N_2 + 3HCl$
(k=1.39x10^9 M^{-1}s^{-1})

(9) $NHCl_2 + 2HOCl + H_2O \rightarrow NO_3^- + 5H^+ + 4Cl^-$
(k=2.31x10^2 M^{-1}s^{-1})

Pinellas County Utilities Distribution System Water Quality

The utility's distribution system water quality data of 2008 and 2009 were used to evaluate the effectiveness of breakpoint chlorination on nitrification control. The monthly routine monitoring data of the entire system were summarized for total residual chlorine, free ammonia, nitrite, and heterotrophic plate count (HPC). The results are presented in Figures 2 through 7.

Figure 3 shows the monthly average total residual chlorine of each monitoring site. The peak monthly average total chlorine (3.6–3.7 mg/L) occurred in February 2008 or March 2009. The median and mean total chlorine then gradually decreased by approximately 0.1 mg/L per month through the month before chlorine maintenance. A drop of 0.6 mg/L in monthly average total residual chlorine was observed between March and July 2009. The minimum total chlorine showed a sharp decrease of approximately 2 mg/L for the same period. The utility maintained relatively constant total chlorine at the entry points during this period. The monthly average total chlorine of the treatment plant finished water varied from 4.0 to 4.1 mg/L, and the monthly average total chlorine of the treatment facility finished water varied from 4.2 to 4.4 mg/L between March and July 2009. The total chlorine drop in the distribution system was likely attributed to residual loss caused by chloramines decay and nitrification, which are accelerated at high temperatures. After chlorine maintenance, average and minimum total chlorine gradually increased to the levels before chlorine maintenance as the system temperature gradually decreased.

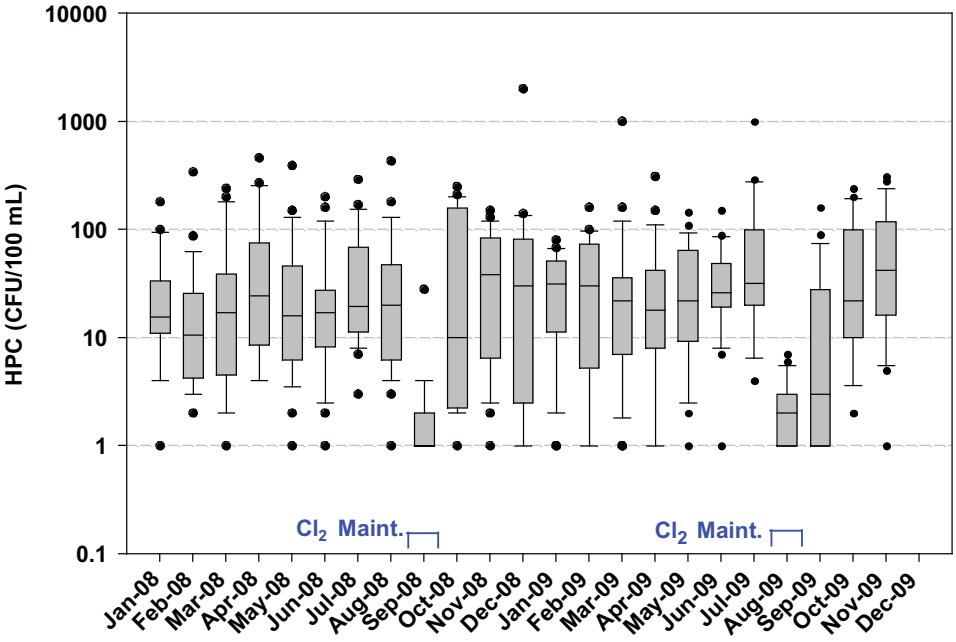
Free ammonia can be released through the chloramines decay. Free ammonia level is a useful parameter for determining the nitrification potential of a system because free ammonia is the energy source of the ammonia oxidizing bacteria. Free ammonia exhibited a similar monthly variation trend as total chlorine. As Figure 4 shows, monthly average free ammonia decreased from 0.35 mg/L in January 2008 to 0.22 mg/L in August 2008. After free chlorine maintenance, free ammonia increased to the levels before chlorine maintenance. A similar trend in free

ammonia concentrations was also observed for 2009. Free ammonia in the distribution system can be affected by many factors. Reactions between chloramines and organic and inorganic compounds affect the chloramines decay rates. Free ammonia uptake and oxidation rates by microorganisms are influenced by temperature, pH, and dissolved oxygen. The results in Figure 3 suggest that the microbial ammonia uptake and oxidation rates may have overtaken the chloramines decay rates during the summer, which reduced free ammonia levels in the system.

Nitrite is the first byproduct of ammonia oxidation by ammonia oxidizing bacteria. Therefore, the nitrite level is one of the most important indicators of nitrification in a system. Any nitrite occurrences exceeding the background levels may suggest the presence of nitrification. Figure 5 shows the monthly average nitrite of each routine monitoring site in 2008 and 2009. No apparent trend in monthly nitrite concentrations was observed. Significant variations in the nitrite levels occurred before free chlorine maintenance. Nitrite levels reduced to baseline condition (0.02 mg/L) during free chlorine maintenance. No elevated nitrite was observed for two months after the maintenance, but elevated nitrite levels occurred in the system after two months. This result is consistent with the literature that says that free chlorine maintenance is effective at inhibiting nitrification, but nitrification is likely to return within several months after the return to chloramines, particularly in systems having warm temperatures throughout the year (Carrico et al., 2008).

Heterotrophic plate count (HPC) is a measure of microbiological activity within the distribution system. Figure 6 presents the monthly average HPCs of each site in 2008 and 2009. Free chlorine maintenance effectively reduced the microbiological activity in the distribution bulk water as evidenced by the considerable drop in mean and median HPCs during maintenance. However, the mean and median HPCs levels returned to prechlorine maintenance levels within one to three months. No apparent HPC trend was identified under normal chloramination operations. The majority of the monthly mean and median HPCs were between 10 and 100 cfu/mL.

The utility performed a nitrification study from July 2008 to October 2009. Total chlorine, monochloramine, free chlorine, free ammonia, and nitrite were monitored biweekly for selected distribution sites and storage tanks. Multiple nitrification episodes



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Whiskers (error bars): 10 percent and 90 percent
Circles: Outliers

Figure 6. Distribution System Routine Site Monthly Average HPCs (2008–2009)

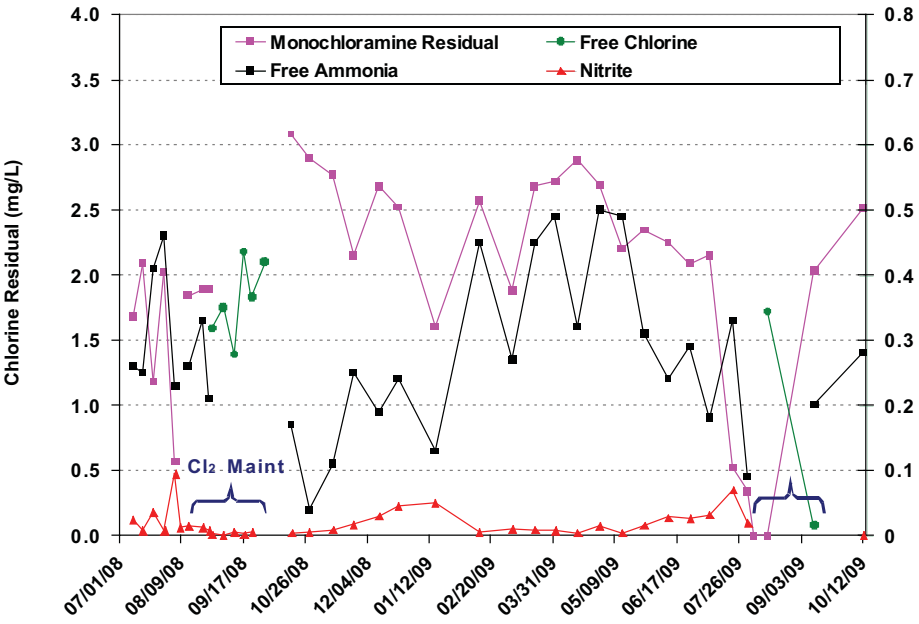

Figure 7. Nitrification Study BAC # 213 (7600 Bayshore Drive) Water Quality

were observed for each site. Figures 7 and 8 present the water quality data for the sampling points at the Bayshore Drive and the Gulf Beach Ground Storage Tanks. The two monitoring sites are located at the south distribution system and have relatively long retention times.

Elevated nitrite levels were generally accompanied by reduced chlorine residuals and free ammonia concentrations, especially when the nitrite concentrations were above 0.1 mg/L. For example, the free ammonia and chloramines residual of the Gulf Beach tank

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decreased to 0.2 and 0.04 mg/L, respectively, while nitrite rose to 0.26 mg/L on March 5, 2009.

Free chlorine maintenance was effective at controlling nitrification at each site. The nitrite level in the Gulf Beach tank remained at low levels for more than five months after the system maintenance was performed in September 2008. However, nitrification returned fairly quickly at the Bayshore Drive sampling site. Elevated nitrite was observed two months after the system maintenance. The results of the nitrification study are consistent with the routine monitoring data of the entire system in 2008 and 2009.

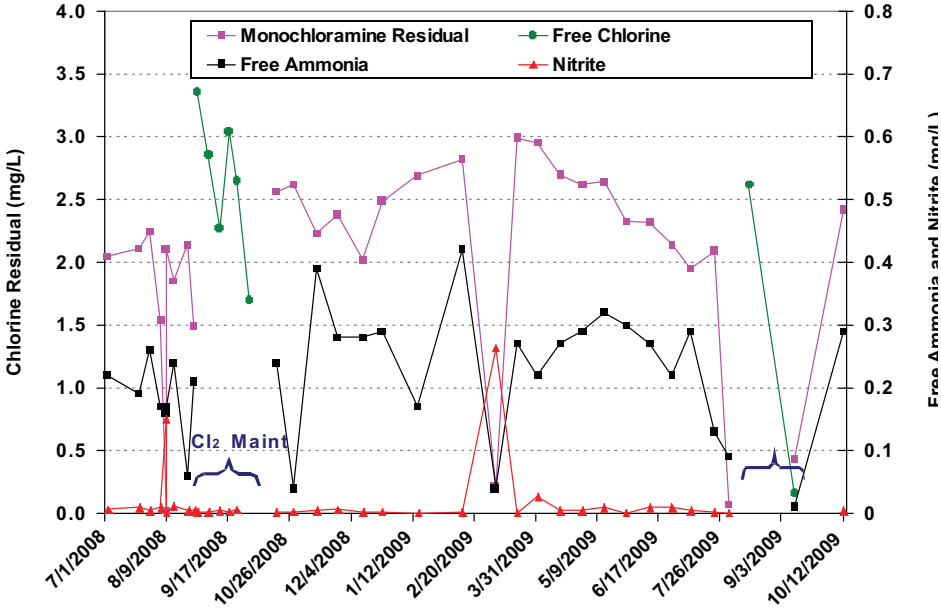

Figure 8. Nitrification Study Gulf Beach Ground Storage Tank Water Quality

Figures 7 and 8 also suggest that a temporary low-residual period occurred at the two sites during the transition from chloramine residual to free chlorine residual, or from free chlorine residual to chloramine residual. For example, the monochloramine residual of the Bayshore Drive site decreased to less than 0.5 mg/L before the free chlorine reached 1.7 mg/L during the initial stage of free chlorine maintenance in 2009. A low free chlorine residual period also occurred at the end of the chlorine maintenance at this site. Similar low-residual transition periods were also observed for the Gulf Beach tank at the beginning and end of the free chlorine maintenance. These temporary low-residual periods were likely attributed to the residual loss caused by the reactions between free chlorine and chloramines.

Total trihalomethanes and five haloacetic acids are currently regulated under the Disinfection Byproduct Rule. Stage 2 of the rule requires the compliance based on locational running annual averages. The compliance limits for trihalomethanes and haloacetic acids are 80 and 60 µg/L, respectively. According to the U.S. Environmental Protection Agency, disinfection byproducts results collected during chlorine-maintenance periods are classified as special monitoring samples and are exempt from regulatory compliance reporting.

Free chlorine maintenance did not cause significant increases in trihalomethanes and haloacetic acids for the monitoring sites that receive treatment plant finished water. The treatment plant uses a ground storage tank as the free chlorine contact tank to meet the disinfection requirements. A relatively high water level is maintained at the ground storage tank, which results in a long free chlorine contact time in the tank. Trihalomethanes and haloacetic acids formation appears to be nearly complete before ammonia is added. Therefore, free chlorine maintenance did not significantly affect the disinfection byproducts concentrations in monitoring sites receiving the treatment plant finished water.

Free chlorine maintenance caused substantial increases in disinfection byproducts for the regional water sites. Figure 9 shows the trihalomethanes data of the regional water monitoring sites from 2002 to 2009. The trihalomethanes levels of the regional water sites were typically below 30

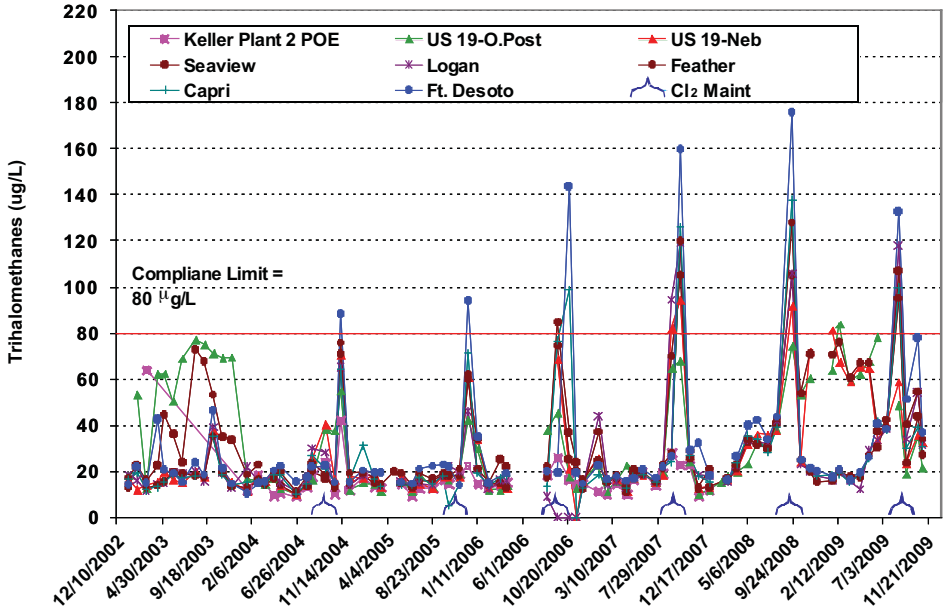

Figure 9. Distribution System Trihalomethanes Monitoring Results–Regional Water Sites

µg/L under normal operating conditions. However, a significant increase in trihalomethanes was observed during the free chlorine maintenance period. The trihalomethanes levels of these monitoring sites were generally higher than 80 µg/L when free chlorine was present in the system. The Ft. Desoto monitoring site had the longest retention time, as well as the highest trihalomethanes concentration during free chlorine maintenance. This suggests that trihalomethanes continued to form in the distribution system as the retention time increased. Despite the trihalomethanes spikes that occurred during free chlorine maintenance, the annual average trihalomethanes in 2009 ranged from 34 to 55 µg/L for each site, with all data included in the calculations.

Regional water haloacetic acids concentrations exhibited a similar trend as trihalomethanes (Figure 10). Low haloacetic acids levels (<20 µg/L) were maintained in the system under normal operating conditions. Free chlorine maintenance increased system haloacetic acids concentrations to 60 µg/L. The annual average haloacetic acids of each

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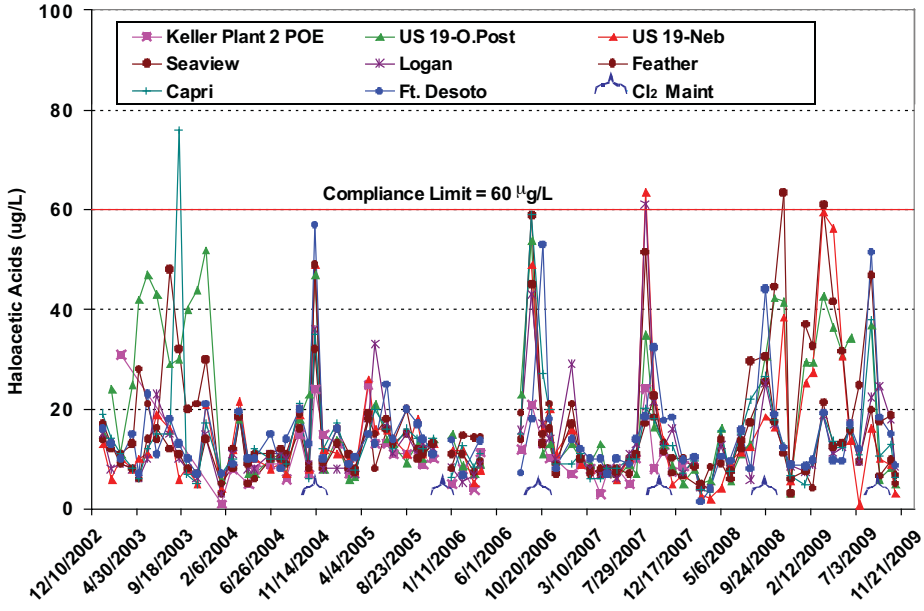

Figure 10. Distribution System Haloacetic Acids Monitoring Results– Regional Water Sites

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site in 2009 were between 15 and 25 µg/L, with all data included in the calculations.

Summary

Nitrification occurrences in the utility's water system have followed the typical response patterns of total residual chlorine loss, accompanied by decreases in free ammonia and increases in nitrite. The average total chlorine gradually decreased by approximately 0.1 mg/L per month from January to the month before chlorine maintenance in the summer. After chlorine maintenance, the average total chlorine gradually increased as the temperature decreased. Annual free chlorine maintenance was effective at inhibiting nitrification in the system, but nitrification typically returned within several months after the return to chloramines.

Based on the utility's experience, an average chlorine-to-chloramines ratio of 2.5 is needed to maintain a free chlorine residual of 3.5 to 4.0 mg/L during chlorine maintenance of the regional water. Breakpoint chlorination caused temporary increases of disinfection byproducts in the system. However, the annual average trihalomethanes and haloacetic acids levels of each monitoring site were well below the maximum contaminant levels with the free chlorine maintenance data included in the calculations.

The utility's nitrification control experience suggests that breakpoint chlorination is able to temporally inhibit nitrification in the system during the free chlorine maintenance. However, free chlorine maintenance alone is insufficient for long-term nitrification control. Comprehensive system monitoring and remedial actions are necessary to successfully control distribution system nitrification.

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