What Happens When Chloramines and Chlorine Meet?

The growing use of chloramines as a secondary disinfectant has created a significant need for training and regulatory review at the state level. This need is even greater when a system using chloramines interconnects with other systems. BY CHARLES G. FARLEY, RYAN GENTZLER, AND COREY W. FLYTHE

BECAUSE CHLORAMINE DECAY and nitrification are rarely linked to health issues, several state regulatory agencies still view these issues as operational nuisances and don't regulate them or require a nitrification response plan. In those states, water companies using chloramines for disinfection may be able to manage these issues within their own systems with total residual chlorine (TRC) levels as low as 0.3 mg/L or 0.2 mg/L. However, low TRC levels (unstable chloramines) entering another distribution system can quickly become a problem.

Some research regarding combined systems (free chlorine and chloramines) describes distribution system blending as problematic but rare. Although such systems pose unique problems at times, more combined systems may exist than previously thought. As more larger systems make the switch to chloramines, smaller systems may still need to interconnect to them for supplemental water.

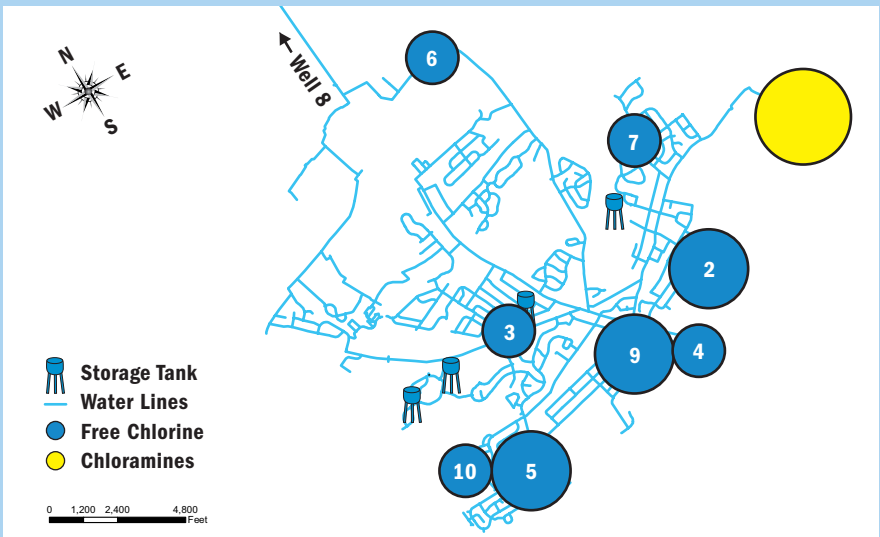
Operators, engineers, and regulatory personnel must know how to detect and respond to signs of chloramine decay and nitrification in distribution systems. The successful operation of the purchasing water company's distribution system relies on the quality of water entering it—both regulated and unregulated.

SYSTEM SPECIFICS

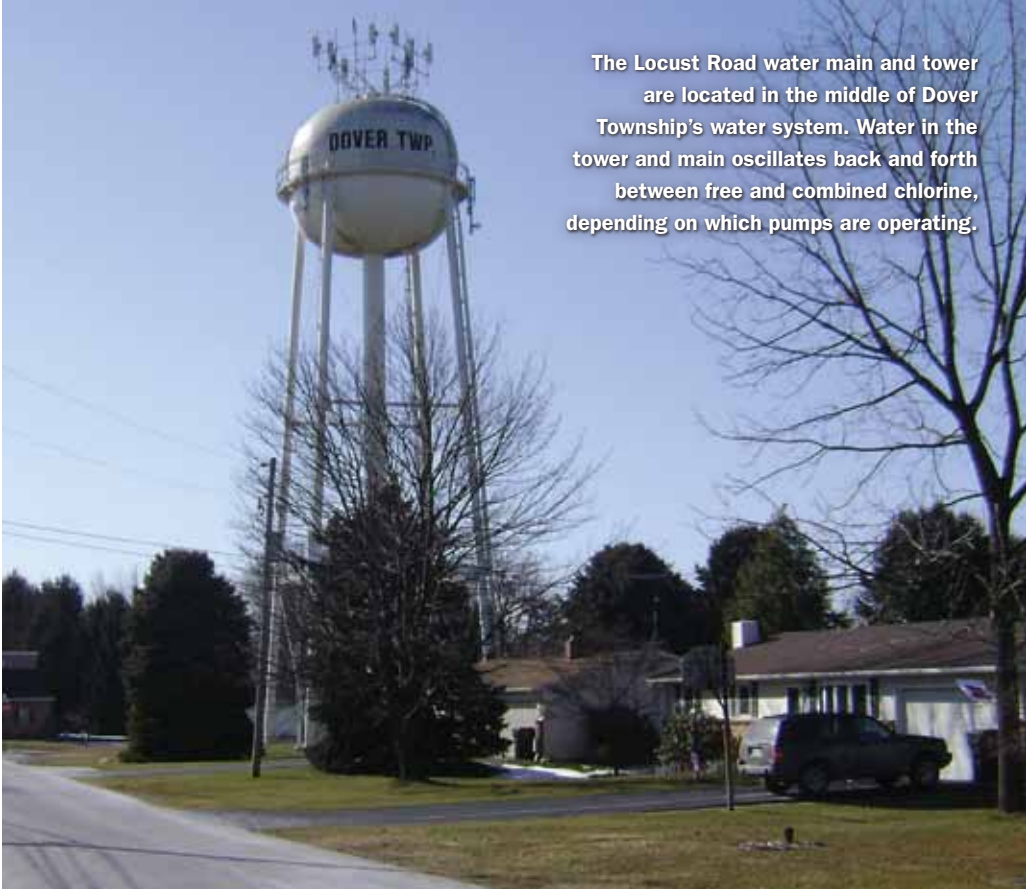
The Dover Township (Pa.) water system has been mixing free chlorine and chloramines since 1993. The township's water system is located in south-central Pennsylvania, a few miles northwest of the city of York. Current water usage is about 1 mgd. The water system consists of 10 entry points (nine groundwater and one surface purchased-water source), five storage tanks, and two pump stations (Figure 1). In 2007, the water system had about 66 miles of 6–8-in. water mains. During a 2010 water main project, about 2 miles of 6–8-in. water mains were upgraded to 10–12-in. mains.

Figure 1. Entry Points Prior to 2006 (Cl_2:Chloramines, 70:30)

The larger blue circles represent wells that produce more than 100,000 gpd. Note the locations of Wells 2 and 7 in relation to the purchased water (chloramines) entry point.



Note: About 0.3 mgd (or 30 percent) of Dover Township's water is purchased from a neighboring water system that disinfects with chloramines. The other 70 percent of the townships's water comes from wells and is chlorinated using sodium hypochlorite.



The Locust Road water main and tower are located in the middle of Dover Township's water system. Water in the tower and main oscillates back and forth between free and combined chlorine, depending on which pumps are operating.

PHOTOGRAPH: CHARLES G. FARLEY, DOVER TOWNSHIP

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Distribution System Residuals. Historically, Dover Township's distribution residuals (TRC) declined in late August and returned to normal in late October or early November. Some distribution residuals declined to less than 0.2 mg/L (TRC). Before 2007, operators monitored free chlorine residuals at groundwater entry points and TRC at all locations within the distribution system. No consideration was given to free chlorine levels in the distribution system.

Taste-and-odor complaints were associated with some of the low-residual areas, which were in the geographical center of the system where chloramine water met chlorinated water. Although main flushing helped maintain residuals and reduced the number of complaints, the amount of flushing seemed excessive.

However, the water system operated in this manner for many years with relatively minor consequences during summer and fall. Typically, 70 percent of the water contained free chlorine and 30 percent contained chloramines, with slightly more purchased water being used during the summer or when a major well was taken out of service. Operations over the years had been problematic but manageable for the most part until a large well was taken out of service in December 2006.

Blending vs. Mixing. A distinction should be made between blending and mixing. Blending is precise mixing by matching flows and/or water quality characteristics. In this article, mixing consists of combining waters with chloramines and free chlorine residuals within a section of a distribution system by whatever means available—for example, using tank levels or timers to operate different pumps. Mixing usually results in some water mains oscillating back and forth between free and combined chlorine. At other times or in other mains, waters are mixed at various points on the breakpoint chlorination curve.

2007 NITRIFICATION EPISODE

In December 2006, one of the largest wells (Well 2) was taken out of service for more than a year for a major upgrade. This required the township to purchase additional water containing chloramines. As a result, the ratio of free chlorine water to water containing chloramines changed from 70:30 to about 56:44. Starting in late summer 2007, operators couldn't maintain adequate chlorine residuals in the center of the system (Figure 2).

While monitoring the loss of distribution system TRC, operators took a closer look at the purchased-water entry point. In the past, this seasonal drop in entry-point (EP) TRC wasn't considered a problem. State regulations allowed 0.02 mg/L combined chlorine (or chloramine) residuals, and the lowest recorded levels

Figure 2. Entry Points Third-Quarter 2007 (Cl_2:Chloramines, 56:44)

Note the loss of Wells 2 and 7, as well as the first mixing zone.

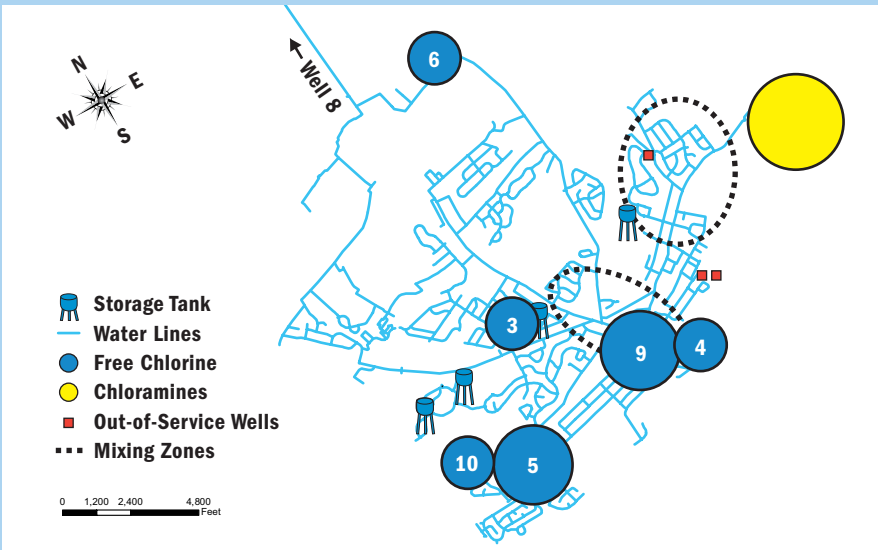
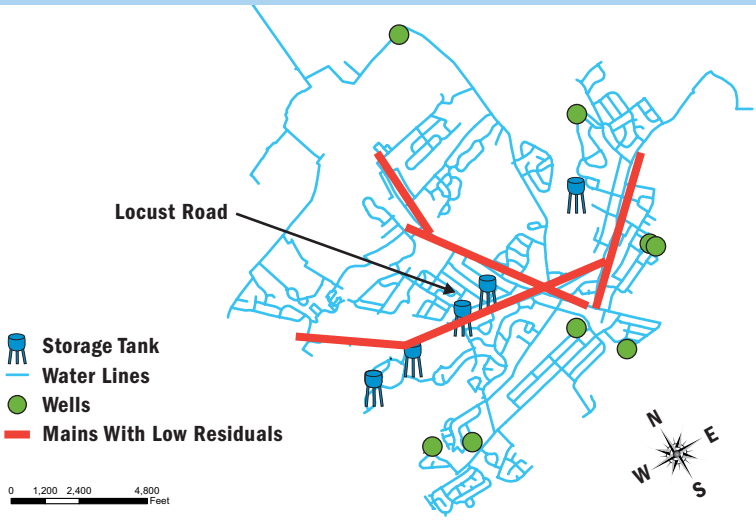


Figure 3. Low TRC, September Through Early November 2007

Mains in the middle of the system have low residuals. The table shows data from the main on Locust Road, which is fed by a mix of waters.



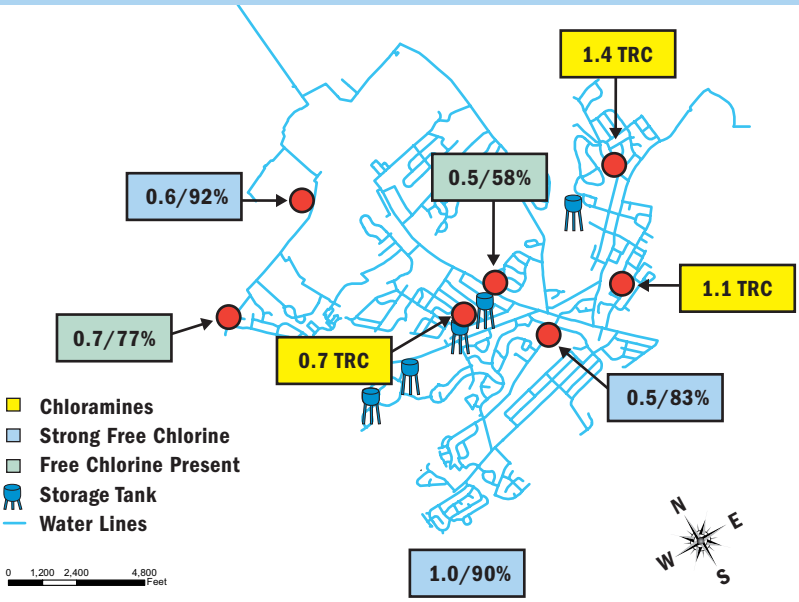
Date	Time	TRC, mg/L	Free, mg/L
Oct. 31	11:30	0.1	0.0
Nov. 1	10:20	0.2	0.0
Nov. 3	23:00	0.2	0.1
Nov. 3	19:00	0.3	0.1
Nov. 4	9:25	0.1	0.0
Nov. 4	19:00	0.6	0.0
Nov. 5	12:25	0.1	0.0
Nov. 5	19:30	0.4	0.0
Nov. 6	21:30	0.3	0.1
Nov. 6	16:20	0.2	0.0
Nov. 7	9:40	0.3	0.0
		Avg. 0.25	

Note: The main on Locust Road fills and receives water from the Locust Road water tower. When Well 3 is operating, chlorinated water is pumped through the main. Virtually no free residual was recorded when Well 3 would have been operating.

entering the system were just less than 0.2 mg/L. However, by the end of third-quarter 2007, a relationship between lower EP TRC and an inability to maintain adequate distribution system residuals became apparent.

Figure 4. TRC, mg/L and Percent Free on Nov. 27, 2007

Residuals were taken less than a week after chloramine levels returned to normal at the purchased water EP. However, Wells 2 and 7 were still out of service, and about 40 percent of the total water used was the purchased water with chloramines.



Loss of Wells 2 and 7. By the end of third-quarter 2007, Well 2 and Well 7 were out of service, and no chlorinated water was entering the distribution system near the chloramine EP. By then, the systemwide chlorine-to-chloramines ratio dropped to 56:44, and, in many areas of the distribution system, operators were unable to maintain a 0.2 mg/L TRC.

In September 2007, operators began monitoring TRC and free chlorine residuals at various problem sites throughout the system. In October, a consultant began daily monitoring of TRC and free chlorine residuals at a location near the center of the distribution system (Figures 3 and 4).

By late October, water operators could only monitor, flush, wait, and try to understand what was happening. Weekly TRC grab samples at the EP ranged from 0.5 mg/L to 0.7 mg/L. It wasn't known whether TRC levels dropped lower than 0.5 mg/L on days when samples weren't collected.

Return of Stable Chloramines. By mid-November 2007, Well 2 was ready to be placed in service, but it wasn't, because of fears that introducing a free chlorine

As more communities consider interconnections with larger water systems, more combined (chlorine and chloramines) systems can be expected.

source while chloramines were unstable might result in total residual loss in many areas because of breakpoint chlorination chemistry. By Thanksgiving, when normal chloramine levels were entering the system, Well 2 was placed online to reduce the amount of purchased water and to help kill or deactivate ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) within the system (Figure 5).

GETTING SOMEONE TO LISTEN

Although there were several internal contributing factors, such as tank water age and low-use mains, reduced TRC (chloramine decay) at the purchased water EP was an external contributing factor.

When township personnel approached the water company regarding the drop in TRC levels at the EP, the water company responded that it has always met Pennsylvania's drinking water regulations (0.02 mg/L TRC). However, a consultant pointed out that Pennsylvania's design standards require maintaining a 1.0 mg/L chloramine residual at all points in the distribution system (Figure 6).

Ultimately, the water company and state regulatory agency agreed that standards might be applicable. As a result, the water company installed an analyzer at the pump house (EP) to record hourly TRC and made plans to install a chlorination facility at its pump house (the township's EP) in 2009.

LESSONS LEARNED

Disinfection By-Products (DBPs). Research on combined systems usually recommends isolation within separate pressure zones, switching an entire system to one disinfectant, and blending or chlorinating to maintain a 5:1 Cl_2:NH_3-N ratio as the best choices for operating combined systems. The few discussions regarding distribution system blending expressed caution when blending in a noncontrolled setting and warned of uncontrolled breakpoint chlorination and DBP formation.

Based on a review of available quarterly data, DBPs are elevated in areas of the system subject to mixing, but there doesn't appear to be a significant DBP-formation problem under current regulations. Additional DBP testing will be necessary to evaluate what effect chlorinating to breakpoint at the EP pump station has on DBP formation.

Distribution System Mixing. When low TRC (as combined chlorine) water enters a distribution system, it usually indicates chloramine decay has occurred and ammonia has been released into the water, which could quickly trigger a reaction with free chlorine.

Observations indicate that distribution system mixing can be reasonably successful if chloramine flows are limited to about 30 percent of total water entering the system, chloramines entering the system are stable, and chloramines come in contact with moderately strong free-chlorine residuals. If not, problems will be more pronounced within areas with greater water age; the worst case could be a major nitrification episode.

When such criteria were met, TRC levels in problem areas were greater than 0.5 mg/L (flushing was sometimes required). Some of the areas had a strong (80 percent or more) free-chlorine presence, other areas had a moderate (40–70 percent)

Figure 5. Initial Mixing Zones

The establishment of mixing zones (in series) may have helped in the past.

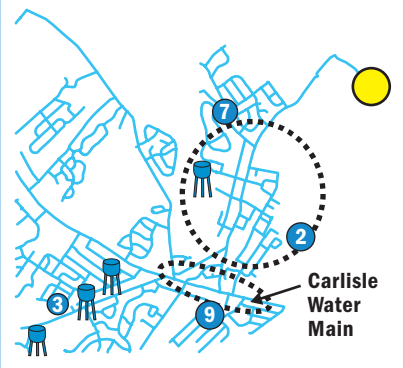
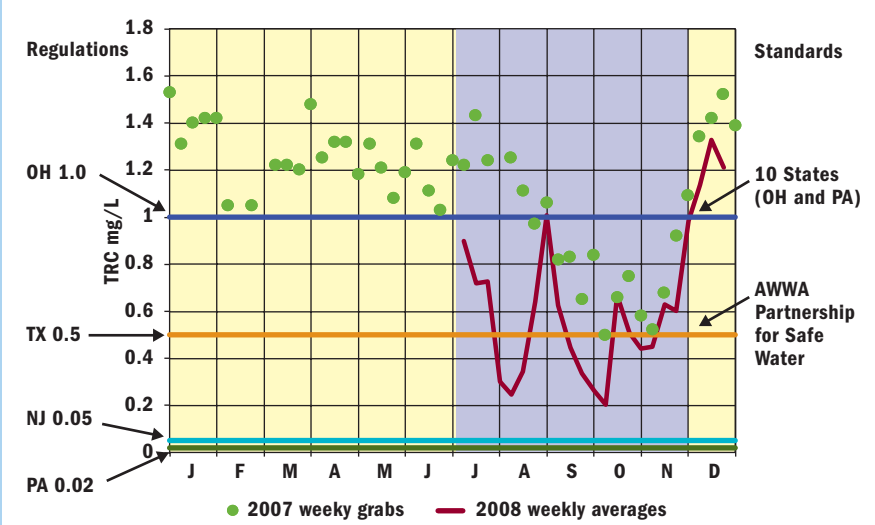


Figure 6. Regulations vs. Standards

State regulations regarding minimum distribution system residuals should reflect state, regional, or industry standards.



Note: The 2007 data points represent weekly grab samples, and the 2008 solid line starting in July shows TRC weekly averages at the EP. EP chlorination was started in 2009.

BEST PRACTICES

MINIMIZE PROBLEMS WITH INTERCONNECTED (COMBINED) SYSTEMS

Although Dover Township has experienced problems with distribution system mixing, those problems can be managed under certain conditions. The following recommendations may be of interest to regulatory staff, engineers, and water operators.

- Keep the chlorine-to-chloramine ratio above 70:30 based on systemwide annual daily average usage. An 80:20 or higher ratio would be better. Remember chloramine decay is likely to occur when groundwater levels are lowest.
- Establish mixing zones where moderate free-chlorine residuals meet stable chloramine residuals.
- Consider the use of a supervisory control and data acquisition system and water quality monitoring to aid water blending based on flows and/or water quality characteristics.
- Don't depend entirely on the purchased source; cut off or reduce the amount purchased in March or April when water tables are high. A month-long changeover to free chlorine is recommended to help kill or inhibit the growth of ammonia- and nitrite-oxidizing bacteria. Be prepared to negotiate this point in the agreement with the water company.
- If your state requires a nitrification response plan, ensure that the water company will notify you when nitrification triggers occur. If your state doesn't require such a plan, make it a condition of your agreement with the water company and jointly develop action and notification plans for when nitrification triggers occur.
- If you already purchase water with chloramines and your state requires only "detectable" distribution system residuals, contact your state regulatory agency. Applicable state standards regarding minimum distribution system disinfectant residual may exist.
- If you're considering a chlorination facility at an entry point (EP) to address chloramine decay, install controls to maintain a 5:1 chlorine-to-ammonia ratio as an option, along with the ability to chlorinate to breakpoint as desired. However, monitor taste-and-odor complaints and run additional disinfection by-product tests in areas near the EP. Remember, chloramine decay is best addressed in the distribution system in which it originated, and EP chlorination should be considered only after other options.
- Operators of distribution systems that mix or blend chlorine and chloramines should incorporate free ammonia, nitrites, and monochloramines into their existing monitoring program to determine breakpoint chlorination status at various locations within the system. Operators should also pay attention to low-use mains, storage tanks, and other areas prone to higher water age.

free-chlorine level, and the remaining areas had a relatively strong TRC with low free chlorine. In those cases, the free-chlorine residual was thought to be from known chloramine interference in the N,N-diethyl-p-phenylenediamine (DPD) test method.

Mixing Zones. A potential aid to successful distribution system mixing may involve having multiple mixing zones and a grid network that exposes fresher chlorinated water to previously mixed or blended water (Figure 6).

CHLORINATION FACILITY

A sodium hypochlorite pump was installed at the pump station and placed into operation in late July 2009. In the weeks before starting the chlorination facility, EP chloramine residuals (TRC) ranged from 0.5 mg/L to 0.6 mg/L. By mid-August 2009, most of the bugs were worked out of the chlorination system, and TRC of 1.25–1.53 mg/L started entering the system. Later, the feed rate was lowered to maintain a 0.9–1.0 mg/L TRC. At the time higher TRC levels were entering the system, a moving breakpoint may have been experienced, but no one understood what was happening. In a subdivision near the EP, TRC levels dropped to near zero, and operators assumed it was a bad batch of DPD reagent. After purchasing new reagent and a period of time had elapsed, results were about 0.9 mg/L as TRC. One or two taste-and-odor complaints were received during the chlorination facility's startup. (Monitoring TRC alone will not indicate if breakpoint has occurred, and downstream conditions can quickly change the water's breakpoint chemistry.)

Currently, the chlorination facility is started in the summer after chloramine (TRC) levels drop and remain less than 1.0 mg/L. Operating setpoints are used to start and stop the pump to maintain 0.9–1.0 mg/L TRC entering the township's distribution system. The pump is usually started sometime in July and operated through October.

OBSERVATIONS

As more communities consider interconnections with larger water systems, more combined (chlorine and chloramines) systems can be expected. Distribution system blending and mixing probably won't be the first choice of operational control when an interconnection is planned. However, blending or mixing may be the least expensive option.

Authors' Note: *The authors acknowledge the contributions of Chester E. Young, Dover, Pa., who helped the Dover Township Water Department through some difficult times, and James Wiga, Dover Township water operator, who conducted most of the main flushing and monitoring during the 2007 nitrification episode.*