Chlorine Dosing at the Ware Disinfection Facility

Bench-scale investigations on chlorine decay led to the development of mathematical models used to investigate a range of chlorine dose scenarios.

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The Massachusetts Water Resources Authority (MWRA) serves three communities via the Chicopee Valley Aqueduct (CVA) from the Quabbin Reservoir (see Figure 1). These communities include Chicopee, South Hadley Fire District No. 1 and Wilbraham. Free chlorine was first added around the mid-1970s during the spring and fall to improve the C factor by controlling biofilm formation. The federal Safe Drinking Water Act Amendments of 1986 placed additional treatment requirements on the system. Chlorine gas was added at Winsor Power Station continuously since the spring of 1992 under a consent order agreement with the Commonwealth of Massachusetts' Department of Environmental Protection (DEP) as a conditional waiver from filtration, with the design and construction of the Ware Disinfection Facility (WDF) as the long-term solution. The WDF came on-line in August 2000 and uses sodium hypochlorite to meet the CT requirement (the concentration of disinfectant multiplied by contact time — CT is usually reported as mg-min/liter) for 3-log inactivation of giardia as met by the chlorine residual measured at the Ludlow Monitoring Station (LMS) just prior to the entry point to the Wilbraham system.

A series of bench-scale chlorine decay tests was performed from September 1999 to August 2000. This testing program formed the basis for the development of a model for chlorine decay kinetics and instantaneous chlorine demand. Monitoring of disinfection byproducts (DBPs) within the three communities (weekly at certain sites) provided bounds to check against chlorine dose, achieved CT and DBP formation. A method for calculating the monthly chlorine dose was developed to explore various operating objectives. These operating objectives included:

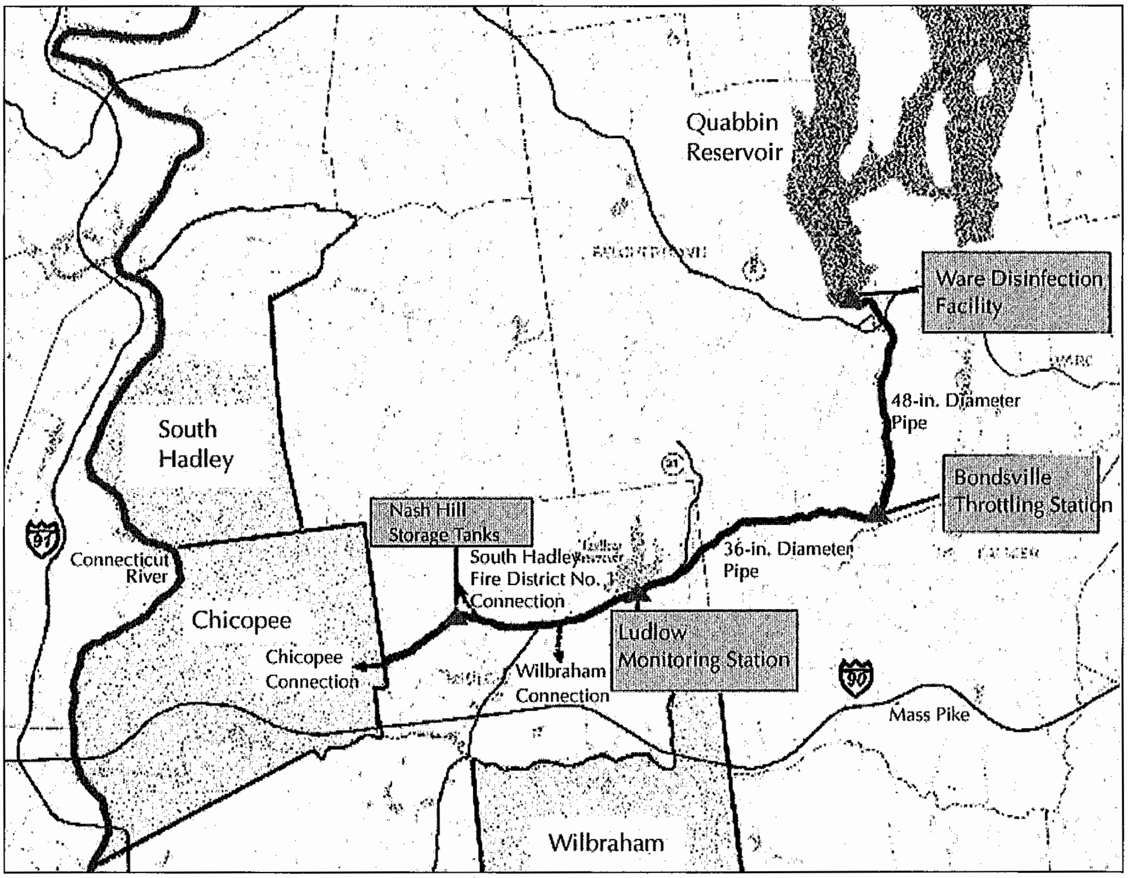

FIGURE 1. Location of the facilities in the study area.

- meeting required CT with a reasonable safety factor;
- minimizing the formation of DBPs; and,
- maintaining a minimum residual at the outlet of Nash Hill storage tanks prior to entry into the Chicopee system.

This approach can be utilized by other utilities using unfiltered surface water. Some of the equations developed will also be applicable for filtered systems using free chlorine (with different rate constants and exponents).

Background

The average daily demand for Chicopee, South Hadley Fire District No. 1 and Wilbraham is close to 10 million gallons per day (mgd); the maximum daily demand is about 20 mgd. The capacity of the aqueduct is 23 mgd. Chicopee is the largest water user of the three communities, and the Nash Hill storage tanks with 25-million gallon capacity were built to even out demand for that system and to provide for covered storage. The WDF is located close to Winsor Dam in Ware. Sodium hypochlorite is added and is paced by flow. There is a pipe loop within the WDF to simulate 20 minutes of contact time after chlorine addition. Two chlorine analyzers (to provide redundancy) monitor the chlorine residual continuously at the loop. The difference between chlorine dose and chlorine measured at the loop gives a measure of the instantaneous chlorine demand. The LMS is located much further downstream (with about 560 minutes of contact time at 10 mgd), just prior to the entry point to the Wilbraham system. The MWRA is using the chlorine residual measured at the LMS to calculate achieved CT (hereafter referred to as one-point time slice). It is possible to take credit for additional CT achievement by including the chlorine residual meas-

TABLE 1.
Dates of Chlorine Decay Tests & Raw Water Quality

Date	pH	Temperature (°C)	UV-254 (abs/cm)	UV-254 MWRA (abs/cm)
9/22/99	6.16	17.5	0.031	
10/6/99	6.85	17.8	0.025	
10/28/99	6.72	14.2	0.024	
11/1/99	6.09	11.5	0.025	
12/14/99	6.30	8.3	0.063*	0.023 on 12/3/00
1/18/00	7.02	3.0	0.025	
2/22/00	6.57	3.2	0.021	
3/21/00	6.35	2.9	0.025	
4/18/00	6.16	6.4	0.028	
5/16/00	6.23	9.0	0.047*	0.022 on 5/15/00
6/20/00	7.15	12.7	0.006*	0.022 on 6/19/00
7/25/00	6.13	13.5	0.036*	0.024 on 7/24/00
8/15/00	6.96	14.0	0.030*	0.025 on 8/14/00

Note: *These UV-254 values are suspect and differ significantly from MWRA measurements made at about the same time.

ured at the delay loop. The CT achieved based on chlorine residuals at both the LMS and the delay loop is hereafter referred to as two-point time slice. The required CT for pathogen inactivation is dependent on temperature, pH and chlorine residual.[1]

Wilbraham adds sodium hypochlorite to maintain a residual of about 0.6 milligrams per liter (mg/L). Sodium silicate is added for corrosion control. South Hadley Fire District No. 1 adds gaseous chlorine to maintain a residual of about 0.3 mg/L and sodium silicate is also added for corrosion control. Chicopee adds gaseous chlorine to achieve a residual between 1 and 1.5 mg/L leaving their water treatment plant. A blend of sodium polyphosphate, sodium bicarbonate and sodium carbonate is also added for corrosion control. Figure 1 shows the location of these facilities and communities.

MWRA is currently using just the chlorine residual measured at the LMS to calculate achieved CT (one-point time slice). A study is currently underway to see if the chlorine addition at the WDF can be optimized to meet residual requirements in all three communities without increasing DBP levels.

Methods

All methods follow the methods established by the American Public Health Association (APHA), the American Water Works Association (AWWA) and the Water Environment Federation (WEF) (unless otherwise noted), and which are currently accepted methods.[2] Details on the chlorine decay tests can be found in Sung *et al.*[3] In particular, ultra-violet (UV) absorption at 254 nanometers was measured using Method 5910 B. Free chlorine residuals were measured by Method 4500-Cl G using a colorimeter. Total trihalomethanes (TTHM) were measured by GC/MS EPA Method 524.2. Haloacetic acids (HAA) were measured by EPA Method 6251 B up until September 2000, and by EPA Method 552.2 beginning in October 2000.

Chlorine Decay Tests

The MWRA has performed weekly tests on chlorine decay at Wachusett Reservoir, its other reservoir serving the metropolitan Boston area, beginning in April 1998 (tests are now conducted on a monthly basis). A

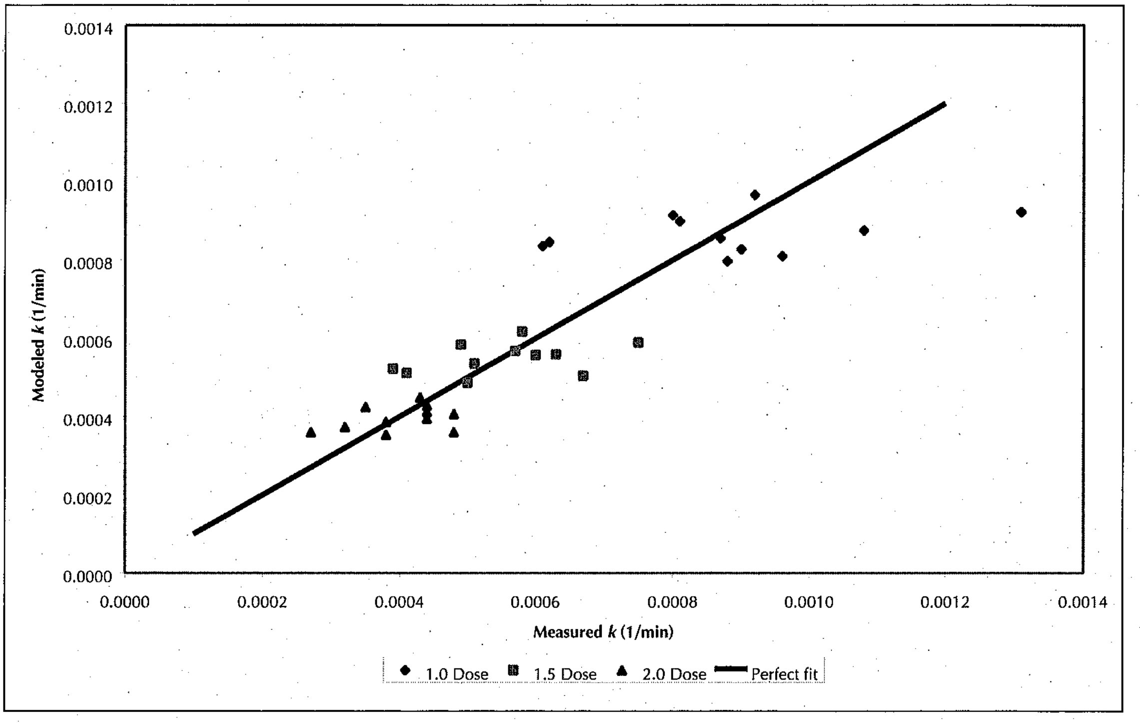

FIGURE 2. Modeled versus measured *k*.

detailed methodology and mathematical model for chlorine decay has been developed for this other reservoir.[3] This methodology and model guided the development of chlorine decay tests performed at Winsor Power Station from September 1999 to August 2000. The actual test dates and some raw water parameters are summarized in Table 1. Each test consists of three chlorine doses at 1.0, 1.5 and 2.0 mg/L. Another study reviewed the results and concluded that the chlorine decay can be summarized by three equations, with chlorine dose as the major variable.[4] The results were fitted as first-order decay curves:

$$Cl_2\ (mg/L) = C_0\, exp(-kt) \quad \textbf{1}$$

The constant C_0 is dose dependent and equals 0.77, 1.22 and 1.70 for initial chlorine doses 1.0, 1.5 and 2.0 mg/L, respectively, because the instantaneous chlorine demand itself is a function of chlorine dose (see Equation 2 below). The unit for the decay constant k is inverse hours and equals 0.0651, 0.0411 and 0.0287 for chlorine doses 1.0, 1.5 and 2.0 mg/L, respectively.

$$Cl_2\ (mg/L) = C_0 exp(-kt) = (C_D\text{-}ID) exp(-kt) \quad \textbf{2}$$

C_D is the chlorine dose and *ID* is the instantaneous chlorine demand. The observation that the instantaneous chlorine demand varies with chlorine dose show that first-order decay is not the most appropriate one for modeling chlorine decay, but the first-order model is adequate for the purpose of this investigation. (Sung *et al.* provide more discussion on the various mathematical models available in the literature for chlorine decay.[3])

The integrated CT achieved can be calculated to be:

$$CT\ (mg\text{-}min/L) = (C_0/k)(1-exp(-k\tau)) \quad \textbf{3}$$

In this formulation k is the chlorine decay rate constant reported in min^{-1} and τ is the travel time in minutes between the point of hypochlorite addition at WDF to the LMS. The integrated CT has not been accepted by the Massachusetts DEP for compliance purposes. The MWRA currently reports on CT compliance by the one-point time slice method.

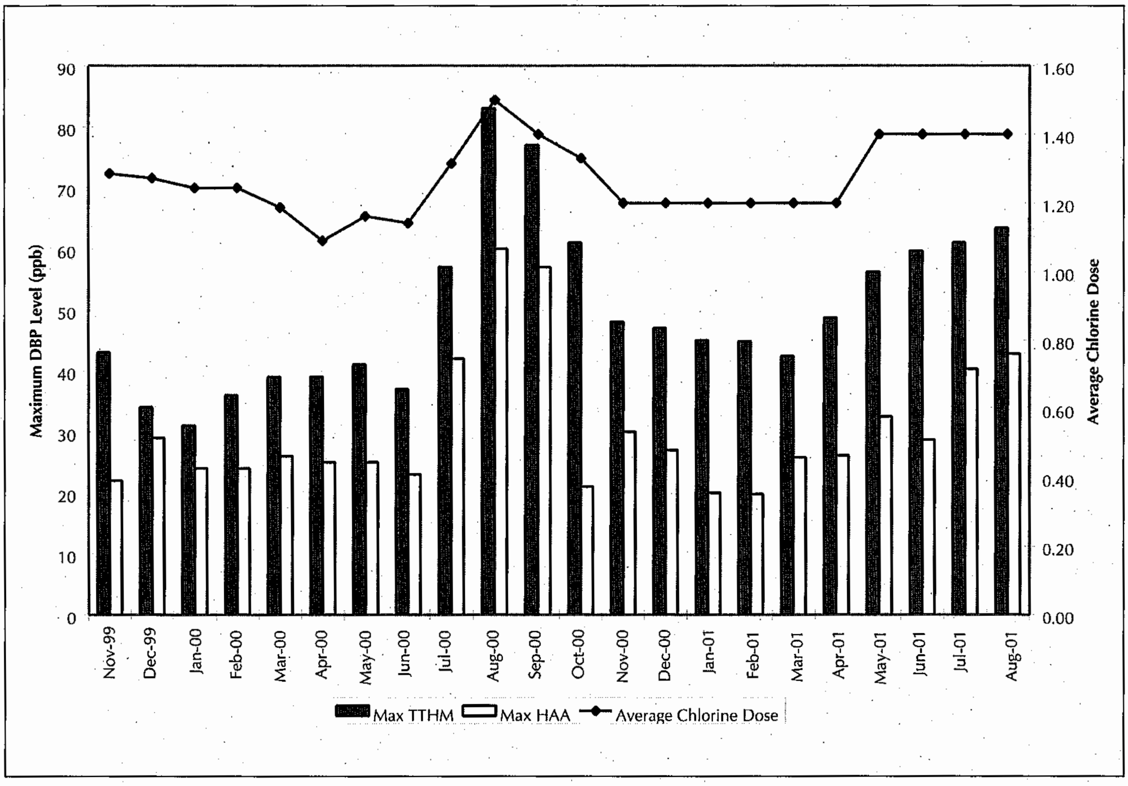

FIGURE 3. Temporal variation in chlorine dose and maximum DBP formation.

In addition, the rate constant is related to water quality measurements and has the form of:

$$k\,(1/min) = 0.013\,(UV\text{-}254)^{0.30}[OH^-]^{0.08}(Cl\ Dose)^{-1.10} \quad 4$$

UV-254 is the absorbance measured at a wavelength of 254 nanometers and reported as cm^{-1}. Li *et al.* discussed extensively the use of UV to characterize the reaction of natural organic matter (NOM) with chlorine.[5] That study reported that NOM molecules are widely represented as containing a few aromatic rings linked via short aliphatic chains. These aromatic rings can be activated by the presence of hydroxyl groups and are thought to be responsible for the majority of the UV absorbance of NOM. In Equation 4, *[OH-]* is the hydroxide concentration in moles/L and related to pH by the ion product of water, *Kw*. The initial pH of the raw water was used for the regression. Chlorine dose is in mg/L. The coefficients were based on a regression of all data from September 1999 to June 2000. However, since UV-254 was shown in Wachusett Reservoir to be the most important parameter to predict chlorine decay, the MWRA-measured UV-254 values were substituted for those days when another study reported that the UV-254 levels were unusual.[4] The regression of all 33 experiments is shown in Figure 2 and r^2 of the regression was 0.77. The errors in *k* using the equation for July and August 2000 conditions were in general less than 25 percent. (The regression is actually improved [by the r^2 criterion to 0.80] when the UV-254 values from the other study are used because they have higher highs and lower lows; however, the errors in *k* would have increased to about 30 percent.) The MWRA and the Massachusetts DEP are conservative in meeting required CT. Therefore, a high safety factor is usually employed (in this study a safety factor of 1.5 was used — or calculated achieved CT is 150 percent of required CT) and the errors in *k* would be covered adequately.

The instantaneous demand can also be modeled in a similar fashion. However, fur-

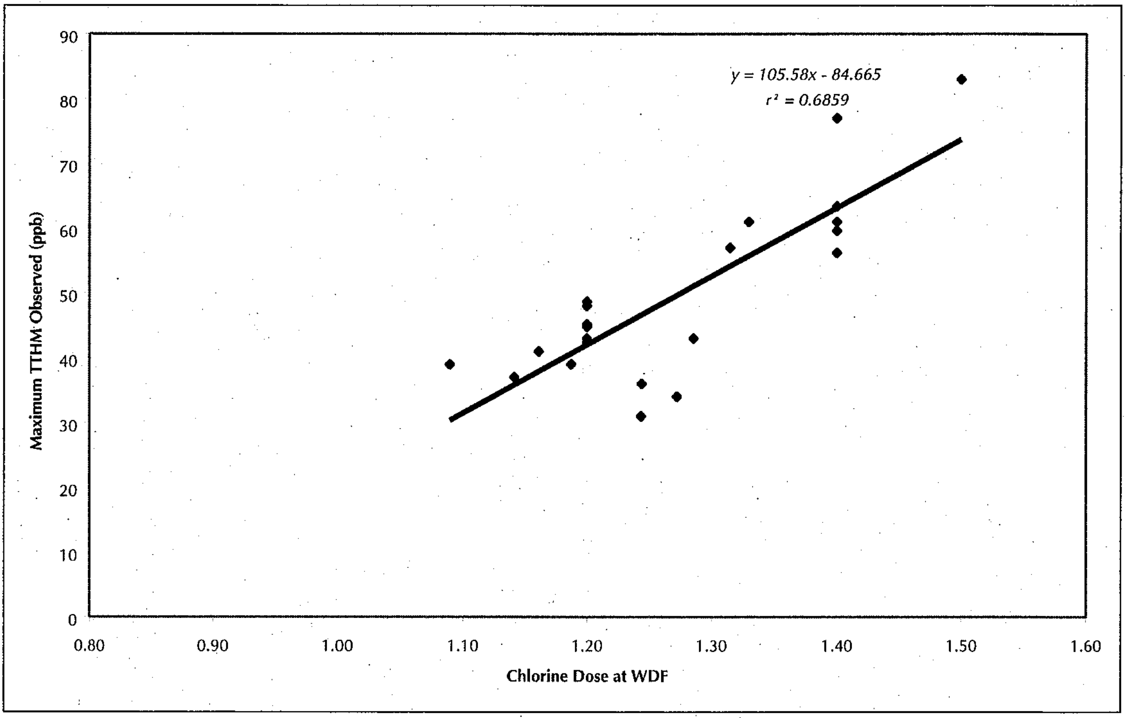

FIGURE 4. The relation between maximum TTHM in the CVA system and chlorine dose at the WDF.

ther analysis of the Quabbin data indicate that the instantaneous chlorine demand is better treated as a constant and is approximately 0.30 mg/L.

Disinfection By-Products

The drinking water maximum contaminant level (MCL) for TTHM and HAA was lowered on January 1, 2002, to 80 and 60 parts per billion (ppb) based on running quarterly values, respectively. These new MCLs are down from current values of 100 and 80 ppb, respectively. The three CVA communities have monitored for DBP levels since the beginning of continuous chlorination in the spring of 1992. Historical values of TTHM levels have reached 100 ppb on several occasions at different locations. The MWRA initiated weekly and monthly monitoring of DBP for process control beginning in November 1999. HAA levels were also monitored. The highest TTHM levels tend to be observed at the South Hadley Marina and Wilbraham Soule Road School. The highest HAA levels tend to be observed at the Nash Hill tank and the Chicopee wastewater treatment plant. The maximum observed DBP levels are shown in Figure 3 along with the actual chlorine dose. Chlorine dose prior to the start-up of WDF are estimated because the actual flow in the CVA could not be accurately measured before the WDF. The increase during July and August 2000 is due to increases in the chlorine dose to 1.6 mg/L. The chlorine dose was increased due to unusually high total bacteria counts in the raw water (fecal coliform was not detected during this period). Figure 4 shows the relation between the maximum TTHM observed at the South Hadley Marina as a function of chlorine dose at the WDF. This figure shows that TTHM levels should not exceed 80 ppb if the chlorine dose is kept less than 1.5 mg/L. Control of the TTHM levels will also lead to control of HAA levels.

Proposed Methodology for Calculating the Chlorine Dose

Figure 5 shows the required CT (averaged monthly) from the Wachusett Reservoir, which has a longer observation period, as well

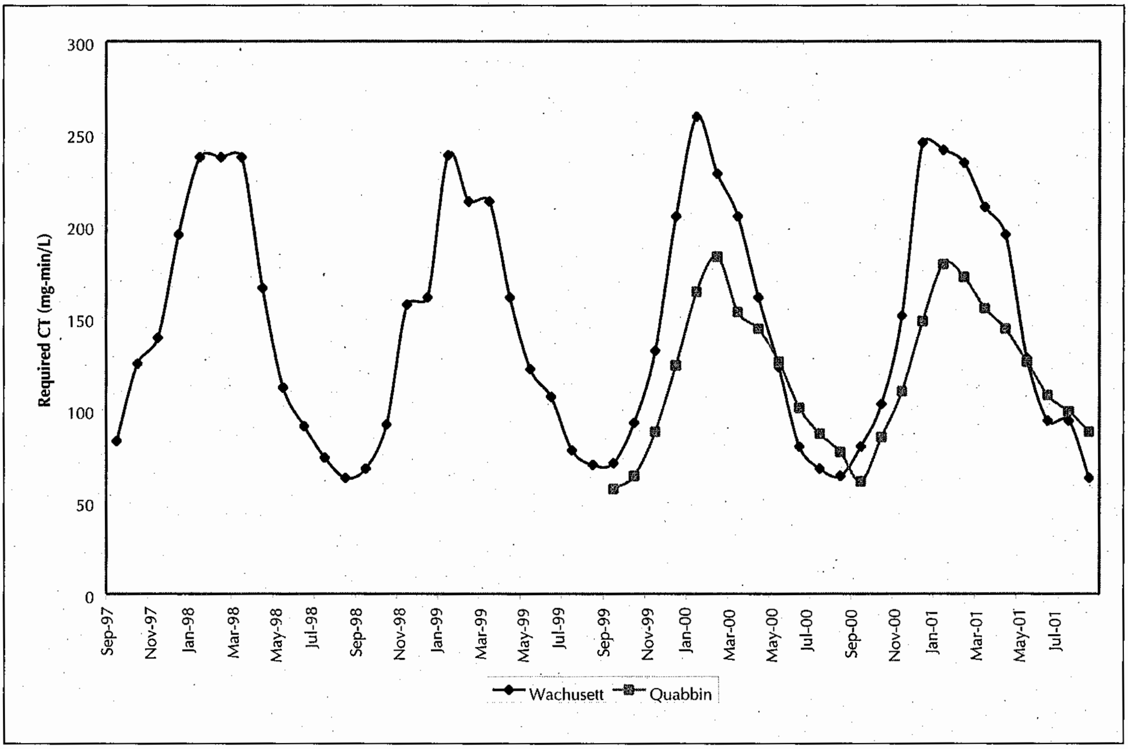

FIGURE 5. Variations in monthly averaged maximum required CT for 3 log inactivation of giardia.

as the Quabbin Reservoir. The required CT is basically driven by natural temperature variations. Quabbin water is taken from a deep location and the temperature is less variable. There can be relatively large variations on an individual day when the reservoir overturns, but in general the average monthly required CT is very regular.

Achieved CT can be calculated using either an integrated approach with Equation 3 or time-slice using Equation 2 to predict chlorine residuals at the LMS. Historical values for water demand, UV-254, pH and temperature can be used to calculate k and contact time. As an example, historical data from September 1999 to December 2000 were used to generate required CT and k. An initial demand of 0.4 mg/L was used to be conservative (jar tests showed about 0.3 mg/L). A peaking factor of 1.5 was used to estimate maximum flow from average flow conditions. Actual flow measurements from September 2000 to August 2001 show that the maximum daily flow is usually less than 130 percent of average daily flow, although on very hot days the maximum peak flow can reach as high as 188 percent of average daily flow. The required chlorine doses that would be necessary to achieve 150 percent (safety factor) of the required CT was calculated. Figure 6 shows the calculated chlorine doses based on these assumptions and one-point time slice CT calculation. The calculated range of chlorine dose was from 0.8 to 1.2 mg/L. The actual dosages were from 1.1 to 1.6 mg/L and reflected different operating objectives. For example, the chlorine dose was elevated at 1.5 mg/L in September 1999 due to being conservative, since the flow measurement at the time was not very reliable. The chlorine dose was again raised from July to September 2000 during the start-up of the WDF. This augmentation was done to "clean out" the CVA in case there was any bio-film formation and to mitigate the elevated bacteria levels observed in the raw water. Table 2 compares the model chlorine dose with the actual chlorine dose for the period of August 2000 to January 2001. The actual percentage of

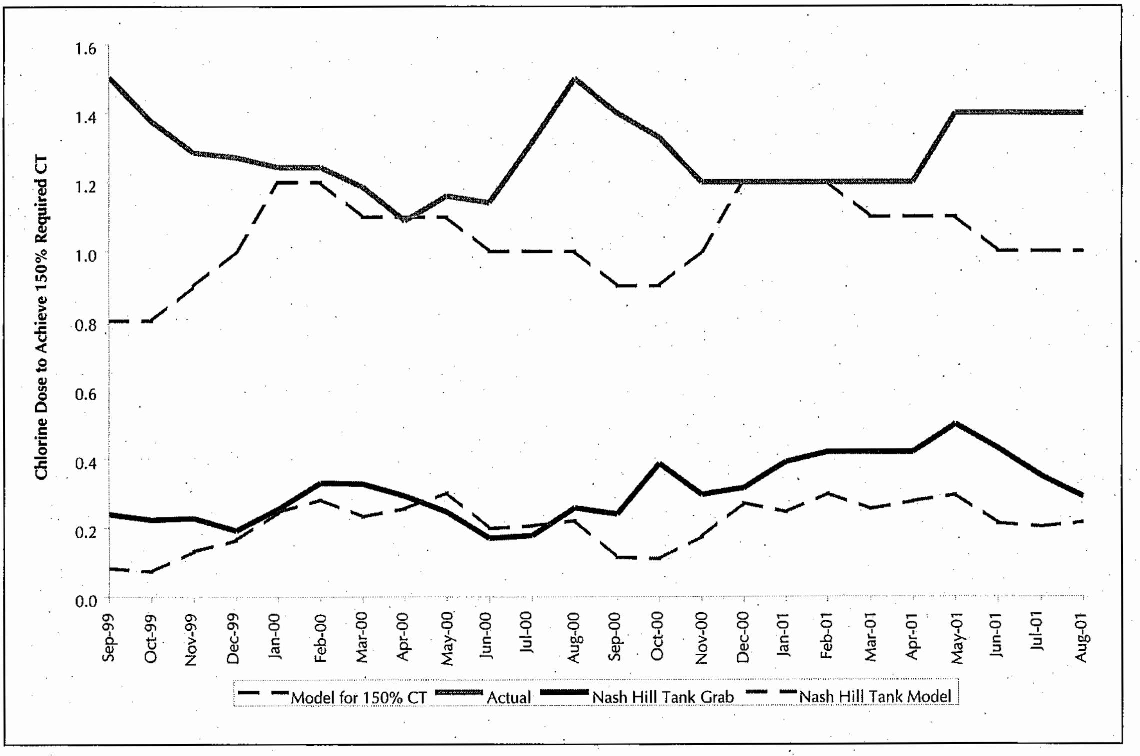

FIGURE 6. Model chlorine dose versus actual chlorine dose for the WDF.

achieved versus required CT is also shown. It varied from 185 to 340 percent, higher than the 150 percent that was adopted for the calculated chlorine doses.

Alternatively, a constant 1.2 mg/L dose could be adopted for operating purposes. This dose would produce DBP levels below regulatory concerns. The Chicopee water department has requested that the MWRA maintain a constant chlorine residual leaving the Nash Hill tanks to help them better operate their residual disinfection system. A level of 0.2 to 0.3 mg/L was deemed to be optimal. The chlorine decay data can also be used to estimate the total detention time from the WDF to the Nash Hill tanks if both the decay constant and detention time were known. Detention time and rate constants were calculated from operating data gathered from September 2000 to August 2001. The rate constant was calculated from daily grab samples of residual chlorine at the delay loop and the LMS. The daily detention time was calculated from this rate constant and ratio of residual chlorine at the LMS and the residual leaving the Nash Hill tanks. These daily values were averaged for the month. The daily retention time ranged from 25 to 38 hours. These monthly values were adopted for back calculations of the minimum residual leaving the Nash Hill tanks with 0.3 mg/L adopted as the instantaneous chlorine demand and the recommended chlorine doses (also shown in Figure 6 along with actual averaged grab samples). The calculated residual at Nash Hill tanks can drop to 0.02 mg/L at low WDF doses of 0.8 mg/L. A chlorine dose of 1.2 mg/L at the WDF would ensure a reasonable level of residual leaving the Nash Hill tanks.

Conclusions

Bench-scale investigations on chlorine decay in Quabbin water have led to development of mathematical models. These models can be used to investigate the chlorine dose necessary for meeting different operating objectives. It was shown that a chlorine dose of 0.8 to 1.2 mg/L (varied monthly to match required CT) was sufficient for meeting pathogen inactivation and minimizing TTHM

TABLE 2.
Model Chlorine Dose Versus Actual Operations

Month	UV-254 (abs/cm)	pH	Minimum Contact Temperature (°C)	Required Time (min)	Model Chlorine Dose for CT (mg-min/L)	Actual Chlorine 1.5 Safety (mg/L)	Actual Achieved CT/ Dose (mg/L)	Required CT (%)
8/00	0.026	6.8	13.8	444	90	1.0	1.5	200
9/00	0.026	6.7	16.5	413	72	1.0	1.4	340
10/00	0.024	6.8	15.4	456	85	0.9	1.3	279
11/00	0.023	6.9	10.7	496	110	0.9	1.2	239
12/00	0.022	6.8	7.4	510	148	1.0	1.2	181
1/01	0.021	6.9	3.0	509	179	1.2	1.2	185
2/01	0.021	7.0	1.9	518	172	1.2	1.2	244
3/01	0.021	6.4	2.4	518	155	1.1	1.2	257
4/01	0.021	6.8	4.4	478	144	1.1	1.2	277
5/01	0.021	6.7	9.1	331	127	1.2	1.4	368
6/01	0.023	6.8	10.4	351	108	1.1	1.4	330
7/01	0.024	7.2	10.8	338	99	1.1	1.4	320
8/01	0.026	7.0	12.7	336	88	1.0	1.4	363

formation. A constant dose of 1.2 mg/L could be adopted to ensure a certain minimum chlorine residual leaving the Nash Hill storage tanks. The MWRA is currently adding 1.4 mg/L at the WDF to see whether this dose can help South Hadley Fire District No. 1 and Wilbraham with their own disinfection process. A program to monitor chlorine levels at the systems' entry points and distribution network for DBP levels and achieved CT was initiated in July 2001.

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