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PREDICTING CHLORINE RESIDUALS AND FORMATION OF TTHMS IN DRINKING WATER

By Robert M. Clark,¹ Member, ASCE, and Mano Sivaganesan²

ABSTRACT: Chlorination is the most widely practiced form of disinfection in the United States. It is highly effective against most microbiological contaminants. However, there is concern that the disinfection by-products (DBPs) formed by the use of chlorine might be carcinogenic. One class of DBPs that are formed and the only class of DBPs that currently are regulated are total trihalomethanes (TTHMs). Therefore, much effort is being expended in developing models that can be used to predict both TTHMs and chlorine residual levels in treated drinking water. This paper presents a model that predicts both TTHMs and chlorine residuals based on the consumption of chlorine and can be used to assist in evaluating the complex balance between microbial and DBP risks associated with disinfecting drinking water with chlorine. The parameters of the model have been found to be functions of total organic carbon, pH, temperature, and initial chlorine residual level. Bromide and the subsequent formation of brominated by-products were not considered in this paper.

INTRODUCTION

Most municipal water supplies in the United States practice some form of disinfection to prevent waterborne infectious disease. These disinfectants may include chlorine, chloramines, ozone, or chlorine dioxide. Frequently, one disinfectant may be used as a primary disinfectant followed by another. In 1974 chloroform, a product of the reaction of chlorine and naturally occurring organic matter, was identified in disinfected drinking water. Since that time a number of other disinfection by-products (DBPs) have been identified including trihalomethane (THMs), by-products other than chloroform (e.g., bromodichloromethane) such as haloacetic acids (HAAs), haloacetonitriles, halo ketones, and haloaldehydes. All disinfectants are reactive and ozone, chloramines, and chlorine dioxide result in both organic and inorganic by-products. More than 500 DBPs have been identified in tap water (Clark et al. 1994).

Over 200,000,000 people in the United States are exposed to disinfected drinking water. Chlorine is a highly effective disinfectant and U.S. practice is to maintain a minimum chlorine residual in distributed water. Chlorine is the most widely used disinfectant in the United States and research has focused on exposure issues related to chlorinated drinking water. Therefore, a key issue is the complex issue of balancing the microbial and DBP risks associated with disinfecting drinking water (Clark et al. 1994).

By-product concentrations vary both spatially and temporally within a distribution system. These variations are caused by source water quality variability, variations in water-treatment efficiency, and the dynamic nature of by-product formation during distribution. Two- and fourfold differences may occur within a water distribution system and the pattern of by-products from different sources can vary significantly over the course of a day as well as during a year (Clark and Adams 1993).

The effects of by-product exposure are assumed to be linked to both the concentration and the nature of the by-products in the water consumed; so there is a great deal of interest in

predicting the formation of DBPs during the distribution of drinking water. Water quality variables that affect types and levels of DBPs and that should be considered when predicting the formation of DBPs in drinking water include the following (Pourmoghaddas et al. 1993; Clark et al. 1996):

- Bromide. Distinct chemical species are produced as the concentration of bromide increases. Toxicological studies suggest that different organs might become targets as the concentration of this ion increases.
- pH. Both the distribution and the concentration of by-products vary with pH. For example, the concentration of chloroform increases with increasing pH, whereas the concentration of trichloroacetic acid increases.
- Natural organic matter. Water sources vary widely in their natural organic matter concentrations, and these variations result in large differences in the yield of all DBPs. Frequently, the magnitude of natural organic matter in drinking water is measured as total organic carbon (TOC).
- Temperature. DBP concentrations tend to increase and to form more rapidly with increasing temperature.
- Other effects. Ammonia present in raw water or added during the treatment process can attenuate DBP formation and result in the preferential formation of certain DBPs.

This paper will develop a mathematical model based on a selected set of these variables to predict chlorine residuals and the formation of total THMs (TTHMs) in drinking water. For purposes of this paper the set of variables to be considered are pH, temperature, and initial concentration of chlorine and TOC. The effect of bromide was not considered in this analysis but will be addressed in future research efforts. The model utilized in this analysis is discussed in the following sections (Clark 1998).

EXPERIMENTAL DESIGN

The experimental conditions associated with the two data sets used in the model development process are shown in Table 1. Data sets 1–36 in Table 1 were generated by the laboratories of the Water Supply and Water Resources Division and data sets 37–42 were created by Pourmoghaddas et al. (1993) as part of his study. The experiments consisted of bench-scale chlorination using humic acids in solution at various levels of pH, temperature, chlorine doses, TOC concentrations, and reaction times.

Water samples were prepared by adding phosphate and borate buffer to Super-Q water in a glass container. For samples 1–36 (Table 1), the reaction solutions were made up at pH 7. For samples 37–42 buffer addition brought the pH of the sam-

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Note. Editor: Byung R. Kim. Discussion open until May 1, 1999. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on December 17, 1997. This paper is part of the *Journal of Environmental Engineering*, Vol. 124, No. 12, December, 1998. ©ASCE, ISSN 0733-9372/98/0012-1203-1210/\$8.00 + \$.50 per page. Paper No. 17201.

TABLE 1. Initial Conditions for Experiments and Values for K , M , and D Estimated from (8) and (17)

Data set (1)	Initial concentration of chlorine (mg/L) (2)	TOC (mg/L) (3)	pH (4)	Temperature (°C) (5)	K (6)	M (7)	D (8)
1	8.1	1.67	5.4	4	0.4	0.05	14.61
2	8.1	1.67	5.4	20	0.65	0.05	14.3
3	8.1	1.67	5.4	36	1.47	0.02	21.53
4	8.1	1.67	7.3	4	0.49	0.07	18.73
5	8.1	1.67	7.3	20	0.66	0.04	25.19
6	8.1	1.67	7.3	36	1.17	0.03	30.65
7	8.1	1.67	11.5	4	0.84	0.21	17.09
8	8.1	1.67	11.5	20	0.6	0.02	39.73
9	8.1	1.67	11.5	36	0.61	0.12	36.53
10	10	0.5	5.4	4	—	—	—
11	10	0.5	5.4	20	0.27	0.04	12.36
12	10	0.5	5.4	36	0.34	0.04	20.81
13	10	0.5	7.3	4	0.18	0.05	18.54
14	10	0.5	7.3	20	0.27	0.04	22.44
15	10	0.5	7.3	36	0.42	0.04	28.82
16	10	0.5	11.5	4	—	—	—
17	10	0.5	11.5	20	0.22	0.06	37.12
18	10	0.5	11.5	36	0.23	0.2	30.75
19	20.1	1.67	4.7	4	0.28	0.03	10.28
20	20.1	1.67	4.7	20	0.45	0.04	7.53
21	20.1	1.67	4.7	20	0.45	0.04	7.53
22	20.1	1.67	7.4	4	—	—	—
23	20.1	1.67	7.4	20	0.42	0.04	17.01
24	20.1	1.67	7.4	36	0.49	0.04	23.86
25	20.1	1.67	11.5	4	0.27	0.02	28.51
26	20.1	1.67	11.5	20	0.36	0.04	26.4
27	20.1	1.67	11.5	36	0.37	0.21	28.15
28	50	1.67	4.7	4	0.39	0.04	3.01
29	50	1.67	4.7	20	—	—	—
30	50	1.67	4.7	36	0.62	0.04	5.68
31	50	1.67	7.3	4	0.31	0.04	6.67
32	50	1.67	7.3	20	0.24	0.04	12.93
33	50	1.67	7.3	36	0.28	0.06	17.1
34	50	1.67	11.5	4	0.3	0.08	8.57
35	50	1.67	11.5	20	0.24	0.04	16.5
36	50	1.67	11.5	36	—	—	—
37	11.5	2.83	5	25	0.91	0.04	23.39
38	11.5	2.83	7	25	0.83	0.18	26.46
39	11.5	2.83	7	25	—	—	—
40	25	2.9	5	25	0.47	0.54	20.62
41	25	2.9	7	36	0.52	0.08	25.75
42	25	2.9	9.4	25	0.41	0.1	37.22

Note: Data sets 1–9 were sampled at times 0, 5, 29, 72, and 144 h. Data sets 10–18 and 28–36 were sampled at times 0, 2, 5, 24, 72, and 144 h. Data sets 19–27 were sampled at 0, 2, 5, 24, 72, and 168 h. Data sets 37–42 were sampled at 0, 6, 48, and 168 h. Data sets 10, 16, 29, 36, and 39 had insufficient data to calculate parameters.

ple to 8.3. The final pH was obtained by the addition of hydrochloric acid or sodium hydroxide. Stock humic acid was added to the samples to obtain the desired level of TOC. Chlorine stock solution was then added to the samples to achieve the initial chlorine levels shown in Table 1. For some data sets values were not obtained at every time. The reaction mixtures typically were 1–2 L. Immediately after mixing, zero time samples were taken by pouring from a larger vessel into a 50-mL serum vial containing an appropriate amount of 0.1 N sodium thiosulphate to halt the reaction by removing chlorine. Samples for storage were taken in a similar manner without sodium thiosulphate. All vials were sealed headspace free with polytetrafluoroethylene-septa immediately after filling. The sealed samples were stored at the indicated temperature in a water bath or incubator at $\pm 0.5^\circ\text{C}$. At the appropriate time the samples were opened and aliquots were transferred to a 30-mL vial containing thiosulphate. The smaller vial (headspace free) then was sealed as described earlier. All preserved samples then were stored under refrigerated conditions. Replicates

were not utilized because of the large number of samples evaluated and the wide range of conditions considered.

Standard method 4500-Cl B was used to measure the residual chlorine for the high-chlorination-dose (25 mg/L) sample. For the remainder of the samples standard method 4500-Cl F was used to measure chlorine residuals. The TTHM analysis was performed by standard method 6232-B. This method has an accuracy of 25% and a precision of 15%. The TOC was measured according to standard method 5310-B (American Water Works Association "Standard Methods" 1995). Humic acid solutions were measured as nonvolatile TOC at various concentrations, which then were chlorinated and held at temperatures of 4, 20, 36, and 25°C (Pourmoghaddas et al. 1993).

MODEL DEVELOPMENT

When chlorine dissolves in water the following reaction generally is assumed:



The HOCl generally reacts with the various components such as organic material in the raw water that make up chlorine demand. Conceptually, this equation may be written as follows:



In (2), if we let the balanced reaction equation be represented by



where A and B = reacting substances; and P = summation of all individual organic species, the product of the reaction. The rate of reaction is given by

$$\frac{dC_A}{dt} = -k_A C_A C_B \quad \text{or} \quad \frac{dC_B}{dt} = -k_B C_A C_B \quad \text{or} \quad \frac{dC_P}{dt} = k_P C_A C_B \quad (4)$$

where $k_A/a = k_B/b = k_P/p$.

Equation for Chlorine Decay

Because both C_A and C_B are changing with time, we must write a relation connecting them in order to integrate the differential equations. If C_{A_0} and C_{B_0} represent the initial concentrations of A and B , respectively, at $t = 0$ and x represents the concentration of A that has reacted, then the concentration of B that has reacted is given by bx/a . Consequently

$$C_A = C_{A_0} - x \quad C_B = C_{B_0} - \frac{bx}{a} \quad (5)$$

and from (5)

$$dC_A = -dx; \quad dC_B = \frac{a}{b} dC_A \quad (6a,b)$$

By substitution in (6) we have

$$dC_A = -k_A(C_{A_0} - x)(C_{B_0} - bx/a) \quad (7)$$

Working through the mathematics yields the following equation (Clark 1998)

$$C_A = \frac{C_{A_0}(1 - K)}{1 - Ke^{-u}} \quad (8)$$

where C_A = concentration of free chlorine in milligrams per liter; K = a dimensionless constant; C_{A_0} = concentration of substance; C_A in milligrams per liter at time = 0; u = a rate constant in minutes; and t = time in minutes.

The value for the rate constant u can be rewritten as follows:

TABLE 2. Pearson Correlation Coefficients for Equation Parameters

Parameters (1)	Initial concentration (mg/L) (2)	TOC (mg/L) (3)	pH (4)	Temperature (°C) (5)
K	-0.35 (0.0370)*	0.38 (0.0229)*	-0.22 (0.1980)	0.31 (0.0613)*
D	-0.55 (0.0005)*	0.02 (0.9005)	0.57 (0.0003)*	0.40 (0.0162)*
M	-0.10 (0.5692)	0.11 (0.5341)	0.34 (0.0416)*	0.28 (0.1039)

Note: p values are in parentheses.

*Linear correlation coefficient is significant at 10% level of significance.

$$u = M(1 - K) \quad (9)$$

where

$$M = \frac{k_A b C_{A_0}}{a} \quad (10)$$

where $M > 0$.

TTHM Formation Equation

A TTHM formation equation was developed using (3). Using (4) and eliminating time as a variable yielding (Clark 1998)

$$\frac{dC_p}{dC_A} = -T \quad (11)$$

where

$$T = \frac{k_p}{k_A} \quad (12)$$

if we let

$$C_p = C_A y \quad (13)$$

and then

$$C_A \frac{dy}{dC_A} + y = -T \quad (14)$$

We can assume $C_A = C_{A_0}$ at $y = 0$; therefore

$$C_p = D(C_{A_0} - C_A) \quad (15)$$

If we let

$$C_p = \text{TTHM} \quad (16)$$

where TTHM = total trihalomethanes; and C_A = chlorine residual in milligrams per liter; and then

$$\text{TTHM} = D \left(C_{A_0} - \left(\frac{C_{A_0}(1 - K)}{1 - Ke^{-u}} \right) \right) \quad (17)$$

where D = dimensionless parameter; C_{A_0} = initial chlorine residual in milligrams per liter; and K , u = parameters from (8).

DEVELOPING A PREDICTIVE EQUATION

The parameters for (8) and (17) were estimated simultaneously for each of the data sets described in Table 1. The SAS procedure PROC MODEL was used (with the weight $w = \text{hours} + 1$) to estimate these model parameters. A two-stage least-squares estimation procedure was used in the "Marquardt-Levenberg" method to estimate the model parameters simultaneously (Marquardt 1963; Amemiya 1974; Johnston 1984; SAS Institute, Inc. "SAS/ETS" 1988). Table 2 contains the values for K , D , and M for the 36 data sets utilized in developing the equation.

Fig. 1 illustrates the best-fit equations based on the data in Table 2 for data set 2. Predictive equations were developed

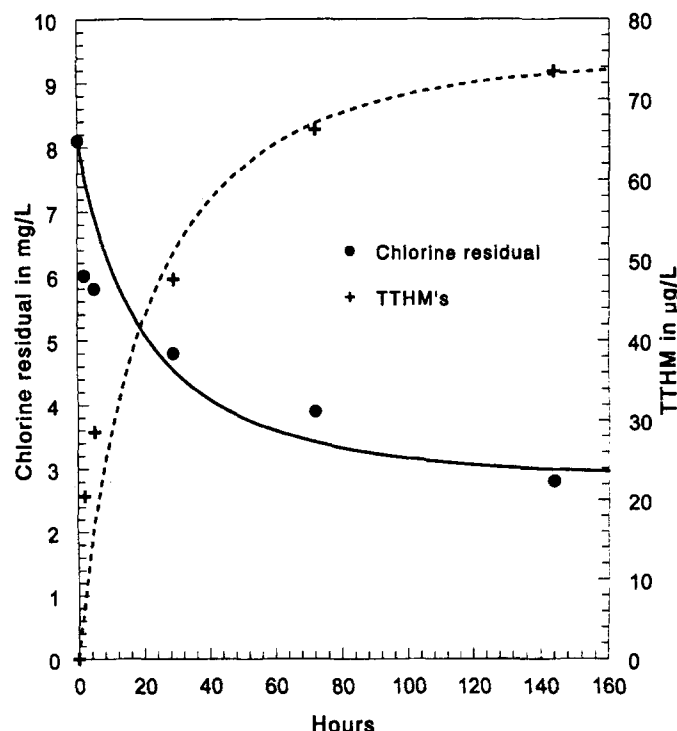


FIG. 1. TTHMs and Chlorine Residuals versus Time for Data Set 2

TABLE 3. Summary of Finished Source Waters Subjected to Chlorine Decay Tests

Data set (1)	Finished water source (2)	pH (3)	Temperature (°C) (4)	TOC (mg/L) (5)	Residual free chlorine (mg/L) (6)
1	FWD-WTP	8.15 ^a	17.9 ^a	1.87 ^b	1.73
2	STLP-A	9.0 ^b	25.0 ^b	3.55 ^b	1.4
3	RRA-B	7.42 ^b	22.2 ^a	0.56 ^b	0.31
4	SLTP-B	8.85 ^a	21.9 ^a	3.55 ^b	0.49
5	50/50 ASLW-B	7.92 ^a	22.1 ^a	2.05 ^b	0.40
6	BWD-WWTP	8.05 ^a	17.4 ^a	0.84 ^b	0.72

^aMeasured in field during sampling study.

^bEPA laboratory study.

for the parameters K , M , and D (Table 2) based on initial chlorine concentration (C_{A_0}), pH, TOC, and temperature (temperature in degrees centigrade). Scatter plots of K , M , and D were made for each of the four independent variables C_{A_0} , pH, TOC, and temperature and were evaluated to show the dependency on these variables. Pearson correlation coefficients for testing linear correlation are given in Table 3.

Parameter Estimation Models

Several functional relationships were explored in an attempt to predict K , M , and D . Even though only some of the cor-

relation coefficients are significant at the 10% level all the independent variables are used for developing a multiplicative model (equivalent to multiple regression model for log-transformed data) for K and D . For M , a linear multiple regression model provided a better fit than the multiplicative model. The contribution from initial chlorine was not significant and therefore was not used in this model but the interaction term $\text{temp} \cdot \text{pH}$ was significant at the 5% level. Thus, the following three models were selected as the general predictive equations for K , D , and M , respectively:

$$K = a_1 \cdot (C_{A_0})^{b_1} (\text{TOC})^{c_1} (\text{pH})^{d_1} (\text{temp})^{e_1} \quad (18)$$

$$D = a_2 \cdot (C_{A_0})^{b_2} (\text{TOC})^{c_2} (\text{pH})^{d_2} (\text{temp})^{e_2} \quad (19)$$

$$\text{Log}(M) = a_3 + c_3 \text{TOC} + d_3 \text{pH} + e_3 \text{Temp} + f_3 (\text{temp} \cdot \text{pH}) \quad (20)$$

The SAS procedure REG (SAS Institute, Inc., "SAS" 1986) was used to compute least-squares estimates of parameters of these multiple regression models. The first two equations were transformed into a linear form by taking the log of both sides of the equation. The estimated parameters for (18)–(20) are as follows:

$$K = e^{0.32} (C_{A_0})^{-0.44} (\text{TOC})^{0.63} (\text{pH})^{-0.29} (\text{temp})^{0.14} \quad (21)$$

$$D = e^{1.49} (C_{A_0})^{-0.48} (\text{TOC})^{0.18} (\text{pH})^{0.96} (\text{temp})^{0.28} \quad (22)$$

and

$$\begin{aligned} \text{Log}_e(M) = & -2.46 - (0.19 \text{ TOC}) - (0.14 \text{ pH}) - (0.07 \text{ temp}) \\ & + (0.01 \text{ temp} \cdot \text{pH}) \end{aligned} \quad (23)$$

The estimated Model R^2 's are 0.71, 0.78, and 0.42, respectively, for these equations.

Validation of Predictive Models

To validate the model it was tested against data collected from two field studies. Using standard statistical techniques the upper and lower 95% confidence intervals were calculated for each parameter. To develop a trace of the upper bounds for (8) and (17), e.g., the value of each parameter (K , D , and M), was estimated at its upper bound for a given value of the independent variables. Each parameter then was set at the upper bound value for all three parameters in (8) and (17) to predict the overall upper bound for a given experimental condition. The lower bound was calculated for the estimating equation in a similar manner.

Field Data Sets

Field data from two studies were utilized (Clark et al. 1994; Vasconcelos et al. 1996) to verify (21), (22), and (23). One study that was a collaborative effort between the American Water Works Association Research Foundation (AWWARF) and the U.S. Environmental Protection Agency (USEPA) involved collecting field data from five sites in the United States and two in France (Vasconcelos et al. 1996). Data also were used from an earlier study conducted approximately 1 year prior to the AWWARF/USEPA study (Clark et al. 1994) by the USEPA. Both studies collected data at the North Marin Water District. North Marin data from the earlier study were designated as study A (NMWD-A). North Marin data from the AWWARF/USEPA study were designated as study B (NMWD-B). Data from the various sites used for this analysis are as follows:

- City of Fairfield Water Department (FWD), Fairfield, Calif.; Waterman Treatment Plant (WTP)
- The NMWD-A, Novato, Calif.—study A; Stafford Lake Treatment (SLTP-A)

- The NMWD-B, Novato, Calif.—study B; Russian River Aqueduct (RRA-B); (SLTP-B); 50/50 blend of aqueduct and Stafford Lake water (50/50 ASLW-B)
- City of Bellingham Water Department (BWD), Bellingham, Wash.; Welcome Water-Treatment Plant (WWTP)

Chlorine reaction kinetics were determined by analyzing the results of bottle tests made on treated waters at each field site. Chlorine disappearance was measured over time in a series of TOC (milligrams per liter) of samples stored in nonreacting containers such as amber glass bottles. These data were used to estimate the rate coefficient associated with kinetic models describing the reactions of chlorine. The TTHM measurements were made using liquid-liquid extraction gas chromatography. Samples were collected in septum-sealed screw-cap bottles with care to omit air bubbles. A reducing agent and acid were added to prevent further TTHM formation after sample collection (Vasconcelos et al. 1996). The TTHM samples were collected from a clear well slightly removed in time from the point of chlorination. Therefore, by the time the sample was taken, a small amount of TTHM already had formed. This anomaly was compensated for in the TTHM models discussed in the following paragraphs. The location and the nature of the waters from each utility are described in Table 4 (Clark 1998). Replicates were made for all samples.

Because the data from the AWWARF were collected in the field and chlorine had already been applied it was necessary to back-calculate the time of initial chlorination to use the predictive models developed previously. To make this calculation, it is assumed that Δt is the difference in time between the actual time the chlorine is added to the water and the time the first sample is taken. Thus, the actual initial chlorine and Δt have to be estimated before predicting chlorine and TTHM values for the field data sets.

Combining (8) with (17) yields the following simple linear regression equation:

$$\text{TTHM} = \alpha - \beta C_A \quad (24)$$

where $\alpha = (D)(C_{A_0})$; $\beta = D$; and C_A = concentration of free chlorine at time = t (minutes). The ratio of the intercept (α) and the slope (β) yields the initial chlorine C_{A_0} .

A simple linear regression (TTHM on C_A) was performed for each of the field data sets to estimate the corresponding initial chlorine C_{A_0} . The parameters K and M then were estimated from (21) and (23), respectively, for each field data set. The estimated values of C_{A_0} , K , and M then are used in (8) to estimate Δt for each data set, which is the time the sample is taken. Note that the value of the free chlorine C_A is known in the foregoing equation at time = Δt .

Δt is added to the recorded time t for each of the field data sets. These new times and the estimated initial chlorine C_{A_0} are used to predict the chlorine and TTHM values for each field data set. The upper and lower 95% confidence intervals were calculated as discussed previously. The results are shown in Figs. 2–7.

Field replicates were collected for TTHM and chlorine residual samples. Figs. 2–7 indicate that data for TTHM analyses exhibited greater analytical variation than for chlorine re-

TABLE 4. Corrected Sums of Squares for Chlorine and TTHM Measurements

Field data set (1)	RSSCl ₂ (2)	RSSTTHM (3)
1	0.0071	27.667
2	0.0743	118.627
3	31152	29.405
4	12.6051	218.639
5	5.2832	81.201
6	0.3147	81.201

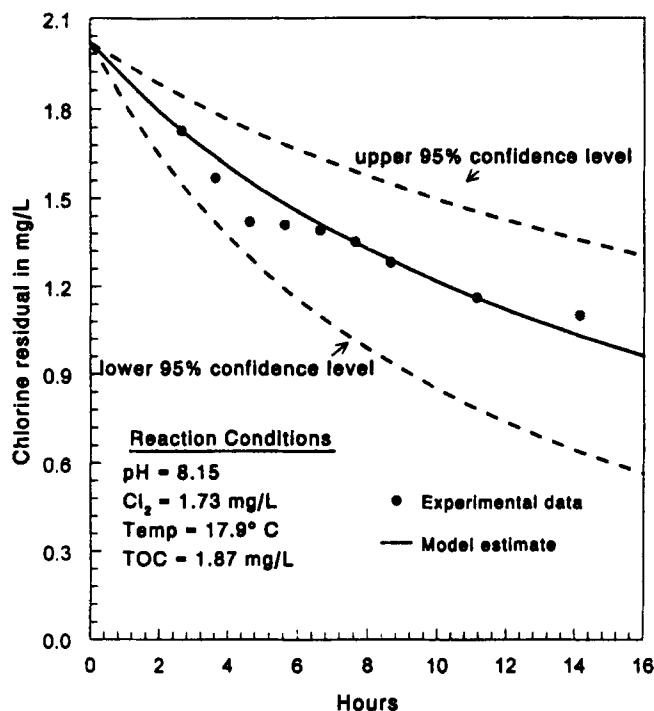


FIG. 2. Predicted Chlorine Residual and TTHM Values for Field Data Set 1

sidual; i.e., data at later hours often showed less TTHM concentration than earlier sampling times. Chlorine demand results are inherently less variable than TTHM because chlorine demand is a relatively simple test to perform in comparison to TTHM analysis (American Water Works Association "Standard" 1995). This is one possible explanation for irregularities seen in the TTHM presentations.

In addition, the process of collecting data in the field can be difficult. For example, chlorine residual data were collected on the spot, at the sampling location, using a handheld instrument and verified in the laboratory. The TTHM samples were collected in the field and transported to a laboratory for analysis. Sampling times were recorded as faithfully as possible,

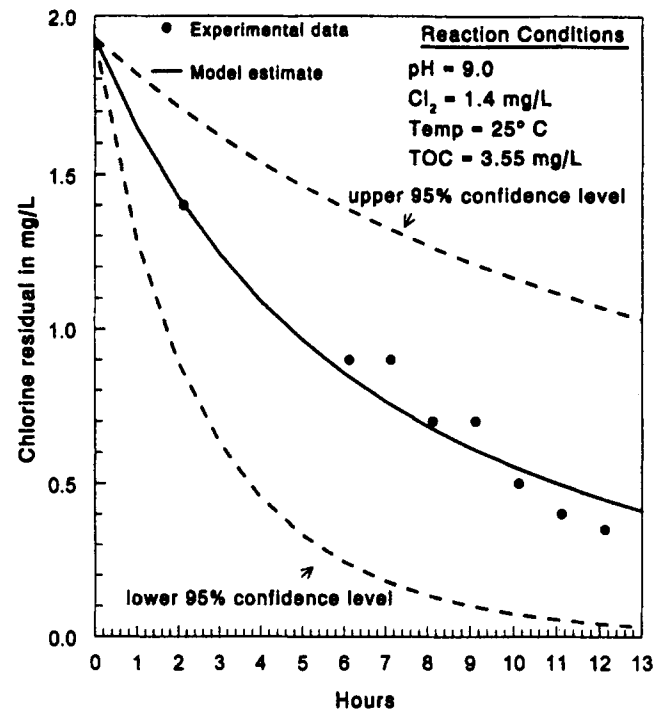


FIG. 3. Predicted Chlorine Residual and TTHM Values for Field Data Set 2

but there may have been some error associated with these values. All of these factors may have had some influence on the results shown in Figs. 2–7. A comparison between the results shown in Fig. 1 and the data in Figs. 2–7 support the concept that laboratory data are more stable than data collected in the field.

To quantify the fact that the errors in the chlorine residual data are less than the errors associated with the TTHM data, a statistical test was applied to both sets of data. The equations applied were as follows:

$$RSSCl_2 = \sum (Cl_t - Cl_p)^2 / Cl_m \quad (25)$$

$$RSSTTHM = \sum (TTHM_t - TTHM_p)^2 / TTHM_m \quad (26)$$

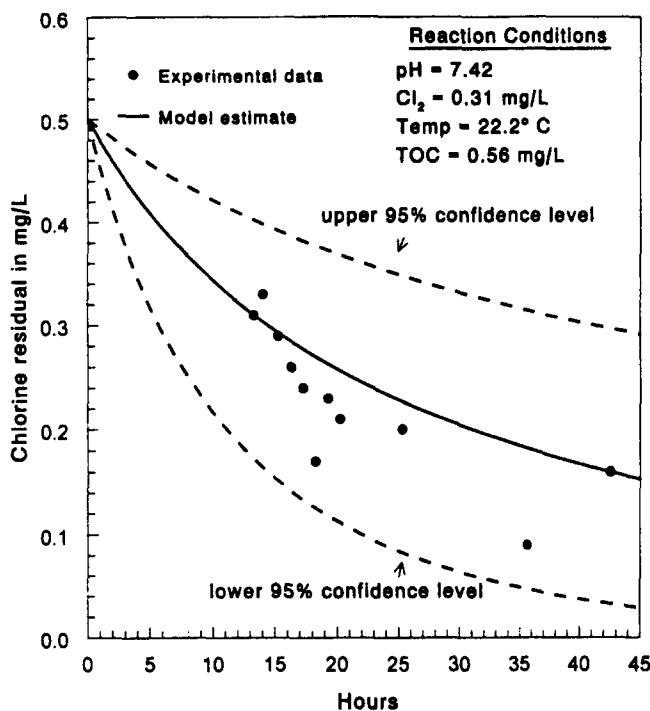


FIG. 4. Predicted Chlorine Residual and TTHM Values for Field Data Set 3

where $RSSCl_2$ = sum of squares of chlorine residuals divided by the mean of chlorine residual values; Cl_r = chlorine residual measurements; Cl_p = predicted chlorine values; Cl_m = mean of chlorine residual measurements ($\sum Cl_r/n$); $RSSTTHM$ = sum of squares of field-measured TTHM values divided by the mean of TTHM measurements; $TTHM_r$ = field measurements for TTHMs; $TTHM_p$ = predicted TTHM values; $TTHM_m$ = mean of field measurements for TTHMs ($\sum TTHM_r/n$); and n = number of observations. The calculated values using (25) and (26) are shown in Table 4.

SUMMARY AND CONCLUSIONS

Rules and regulations established under the Safe Drinking Water Act and its Amendments of 1986 and 1996 have em-

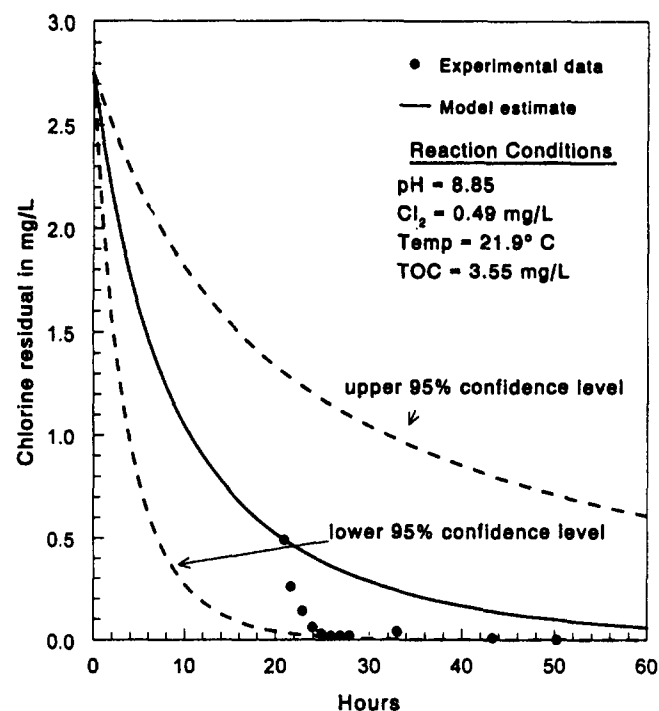


FIG. 5. Predicted Chlorine Residual and TTHM Values for Field Data Set 4

phasized the importance of maintaining disinfectant residuals in drinking water distribution systems. There also is concern over the formation of potentially carcinogenic compounds that result from the application of disinfectants. Chlorine is one of the most commonly used and effective disinfectants in use today. Many investigators have examined the kinetic relationships associated with chlorine decay and DBP formation in drinking water-distribution systems in water.

There is concern over both the exposure experienced by consumers to these by-products and the need to maintain microbial safety in the distribution system. This paper presents models that can be used to predict DBP exposures and chlorine residuals. It was found that the variables pH, TOC, tempera-

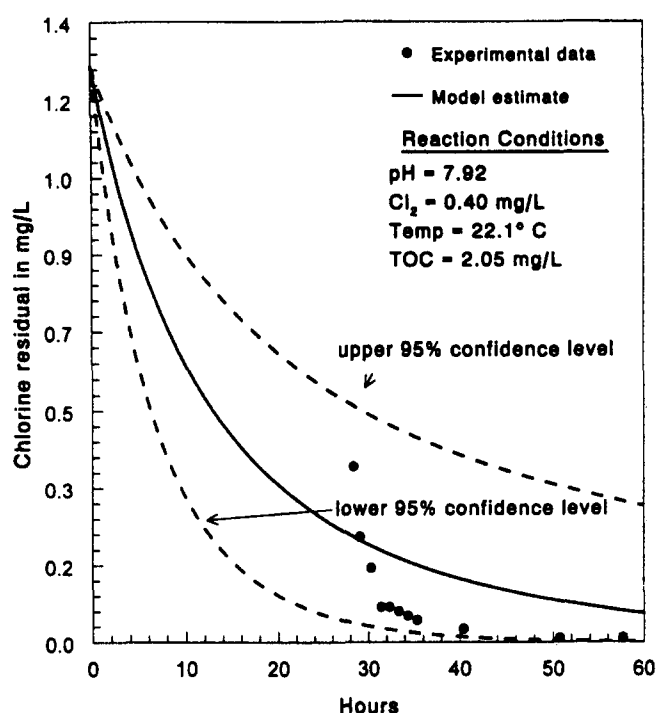


FIG. 6. Predicted Chlorine Residual and TTHM Values for Field Data Set 5

ture, and initial chlorine concentration were correlated with the parameters in the chlorine residual and TTHM formation equations. Based on this analysis, it has been shown that the formation of TTHMs is a direct result of the consumption of chlorine. The data used in this paper was generated under controlled conditions in order to provide a common basis for comparison. However, these equations can be modified to reflect distribution system conditions.

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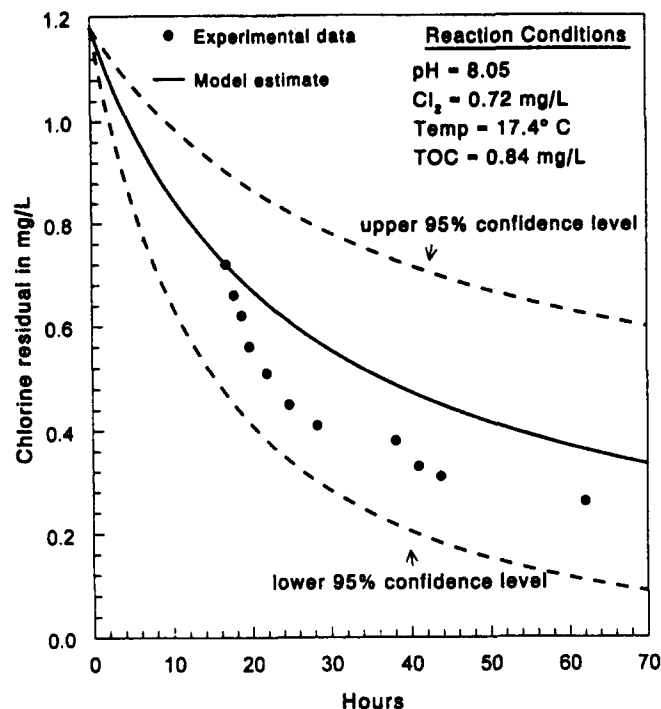


FIG. 7. Predicted Chlorine Residual and TTHM Values for Field Data Set 6

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APPENDIX II. NOTATION

The following symbols are used in this paper:

A = reacting substance;
 a = coefficient of reacting substance A ;
 a_1, a_2, a_3 = regression parameter;
 B = reacting substance;
 b = coefficient of reacting substance B ;
 b_1, b_2, b_3 = regression parameter;
 C_A = concentration of reacting substance A ;
 C_{A_0} = initial concentration of substance A ;
 C_B = concentration of reacting substance B ;
 C_{B_0} = initial concentration of substance B ;
 $C(t)$ = concentration of chlorine at any time;

cly = rate of change of variable indicating ratio of concentration of product P to substance A ;
 c_1, c_2, c_3 = regression parameter;
 D = dimensionless parameter in TTHM equation;
 dC_A = rate of change for concentration of substance A ;
 dC_B = rate of change for concentration of substance B ;
 dC_P = rate of change for concentration of the products;
 dt = rate of change in time;
 dx = rate of change of concentration in x ;
 d_1, d_3 = regression parameter;
 e_1, e_2, e_3 = regression parameter;
 f_3 = regression parameter;
 K = constant that is function of initial concentrations of substances A and B and their coefficients;
 k_A = reaction rate constant for formation of substance A ;
 k_B = reaction rate constant for formation of substance B ;
 k_P = reaction rate constant for formation of products;
 M = positive component of rate constant;
 n = number of observations;
 P = product of reaction between A and B ;
 p = coefficient of products;
 R = ratio of initial concentrations of reacting substances and their coefficients;
 r = formation rate constant;
 T = ratio of rate of change in C_A to rate of change in C_B ;
 t = time;
 u = reaction rate constant;
 x = concentration of A that has reacted;
 y = variable indicating ratio of concentration of product to substance A ;
 α = equation parameter;
 β = equation parameter; and
 Δt = increment of time.