

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/281295441>

Chlorine Demand and TTHM Formation Kinetics: A Second- Order Model

Article in *Journal of Environmental Engineering* · January 1998

DOI: 10.1061/(ASCE)0733-9372(1998)124:1(16)

CITATIONS

202

READS

1,187

1 author:



[Robert M. Clark](#)

United States (US) Public Health Service and US Environmental Protection Agency (Retired)

597 PUBLICATIONS 9,396 CITATIONS

SEE PROFILE

CHLORINE DEMAND AND TTHM FORMATION KINETICS: A SECOND-ORDER MODEL

By Robert M. Clark,¹ Member, ASCE

ABSTRACT: Much effort has been expended in attempting to develop mathematical models for chlorine demand in water and wastewater. Most of these efforts have centered around the use of first-order functions or modifications of first-order functions. Recently there has also been interest in characterizing the formation of total trihalomethanes. These efforts have taken on new meaning because of the importance of maintaining chlorine residuals for microbial protection and concerns over the formation of trihalomethanes in drinking water distribution systems. This paper applies second-order kinetics to describe both of these relationships, using data collected from a recent collaborative study between the EPA and the American Water Works Association Research Foundation. It demonstrates that TTHM formation can be characterized as a function of chlorine demand.

INTRODUCTION

One of humanity's most successful public health interventions is the disinfection of public drinking water supplies to prevent the occurrence of waterborne disease from microbial pathogens. Chlorination of drinking water has been successfully used to inactivate pathogenic organisms since the turn of the century and is the most widely used method of disinfection in the United States today. Currently, more than 200 million people in the United States consume disinfected drinking water. This practice has virtually eliminated serious waterborne disease outbreaks.

Rules and regulations have been established under the Safe Drinking Water Act (SDWAA) and its amendments to ensure that this protection is maintained (Vasconcelos et al. 1996). For example, the surface water treatment rule requires a minimum level of 0.2 mg/L at the entrance to the distribution system. It also requires that a detectable chlorine residual level (or heterotrophic plate count < 500/mL) be maintained throughout the system. However, when chlorinated water is introduced into the distribution system, the chlorine residual tends to dissipate, which may then result in microbiological regrowth, increasing the system's vulnerability to contamination. Three factors that frequently influence chlorine consumption are: (1) reactions with organic and inorganic chemicals (e.g., ammonia, sulfides, ferrous iron, manganous ion, humic material) in the bulk aqueous phase; (2) reactions with biofilm at the pipe wall; and (3) consumption by the corrosion process.

A by-product of chlorination is the formation of total trihalomethanes (TTHMs) in water containing organic precursor compounds, such as humic and fulvic acids. The generation of TTHMs has been shown to be a function of various water quality parameters and chlorination conditions, including total organic carbon, the type of organic precursor, chlorination level, pH, temperature, bromide level, reaction time, and UV-254 absorbance. TTHMs are regulated under the SDWAA (Amy et al. 1987; Clark et al. 1996). Chlorine decay in distribution systems is generally considered to be composed of two components. One component is wall demand; the other is associated with decay in the bulk phase of the water (Clark et al. 1993).

Frequently, chlorine decay in the bulk phase is characterized by a first-order kinetic model as follows:

$$dc/dt = -kc \quad (1)$$

where c = chlorine concentration (mg/L); k = first-order decay constant (min^{-1}); and t = time in minutes. Integrating (1) yields

$$C(t) = C_0 e^{-kt} \quad (2)$$

where $C(t)$ = chlorine concentration (mg/L) at time t ; C_0 = initial chlorine concentration (mg/L); and t = time of reaction (Clark et al. 1993).

Several other types of kinetic models have been used to characterize chlorine decay kinetics. For example, Haas and Karra (1984) evaluated the reliability and performance of five different chlorine decay models: first-order decay, power-order decay (n th order), first-order decay with stable component, power law decay with stable component (n)th, and parallel first-order decay. They found that the parallel first-order decay model—which assumes parallel decay of two components of chlorine residual, one decaying more rapidly than the other—provided the best results. Few models have been developed to predict the formation of TTHMs in chlorinated water (Amy et al. 1987; Clark et al. 1996).

In 1993 a collaborative study between the U.S. Environmental Protection Agency (EPA) and the American Water Works Association Research Foundation (AWWARF) was initiated (Vasconcelos et al. 1996). The study was conducted to gain an understanding of the kinetic relationship between chlorine decay and total trihalomethane (TTHM) formation in water distribution systems. The EPANET distribution network model was used to test and validate several kinetic models based on data collected from the utilities that participated in the collaborative study (Rossman et al. 1994). Controlled tests were conducted at each utility for chlorine decay and TTHM formation. For the chlorine decay tests, samples of water were stored in zero-head-space, darkened bottles at ambient temperature. Individual bottles were then opened at different times, chlorine residuals measured, and the residual values plotted against time. TTHMs were measured using the liquid-liquid extraction process (Vasconcelos et al. 1996). Various chlorine decay and TTHM formation kinetic models were evaluated to find the one that best characterized the data. As in Haas and Karra's (1984) study, chlorine decay models evaluated included: a first-order decay model, an n th order model, a first-order model with a stable component, and a parallel first-order decay model. In Vasconcelos et al.'s (1996) study, the n th order model yielded the best fit in about half the cases and the parallel first-order model yielded the best fit in the other half. A formation potential model was developed for TTHM, similar to the model developed by Clark et al. (1996).

This paper presents alternative models for bulk chlorine decay and TTHM formation based on second-order reaction kinetics. The model shows that TTHM formation can be char-

¹Dir., Water, Supply and Water Resour. Div., Nat. Risk Mgmt. Res. Lab., U.S. Environmental Protection Agency, Cincinnati, OH 45268.

Note. Associate Editor: Makram T. Suidan. Discussion open until June 1, 1998. 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 February 11, 1997. This paper is part of the *Journal of Environmental Engineering*, Vol. 124, No. 1, January, 1998. ©ASCE, ISSN 0733-9372/98/0001-0016-0024/\$4.00 + \$.50 per page. Paper No. 15153.

acterized as a function of chlorine demand. The rate of reaction is assumed to be proportional to the first power of the product of the concentration of two different species. One component is assumed to be hypochlorous acid, and the second represents the constituents in water that cause the "chlorine demand." Among the products of this reaction are the formation of TTHMs.

DATA SOURCES

The model is validated using data collected in the AWWARF/EPA study and in a study conducted approximately one year earlier at the North Marin Water District (NMWD) (Clark et al. 1994). The AWWARF/EPA joint study involved collecting field data from five sites in the United States and two in France (Vasconcelos et al. 1996). The earlier study conducted at the North Marin Water District is designated as NMWD-A and the most recent study is designated as NMWD-B. These sites are as follows:

- United Water Resources (UWR), Harrisburg, Pa.
Oberlin pump station (OPS)
- North Penn Water Authority (NPWA), Lansdale, Pa.
Keystone tie-in (KTI)
Forest Park treatment plant (FPTP)
50/50 blend of Keystone and Forest Park water (50/50 KFPW)
Well W17 (W17)
Well W12 (W12)
- City of Fairfield Water Department (FWD), Fairfield, Calif.
Waterman treatment plant (WTP)
- North Marin Water District (NMWD-A), Novato, Calif.
Russian River aqueduct (RRA-A)
Stafford Lake treatment (SLTP-A)
50/50 blend of aqueduct and Stafford Lake water (50/50 ASLW-A)
- North Marin Water District (NMWD-B), Novato, Calif.
Russian River aqueduct (RRA-B)
Stafford Lake treatment (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)
- Parisienne des Eaux System (PES), Paris, France
5/23/94
5/31/94
6/8/94
6/16/94
- City of Orleans water system (OWS)

Chlorine reaction kinetics were determined by analyzing the results of bottle tests on treated waters at each field site. Chlorine disappearance was measured over time in a series of measurements of total organic carbon (mg/L) in 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. TTHM measurements were made using the liquid-liquid extraction gas chromatographic method. Samples were collected in septum-sealed screw-cap bottles, with care to avoid air bubbles. A reducing agent and acid were added to prevent further TTHM formation after sample collection (Vasconcelos et al. 1996).

For purposes of this study only the systems using free chlorine were used for analysis, which excluded the North Penn Water Authority. No data were available from the OWS and the 5/31/94 study in the PES and TTHM data were not collected for UWR, and the French water systems and no chlo-

TABLE 1. Summary of Finished Source Waters Subjected to Chlorine Decay Tests

| Finished water source (1) | pH (2) | Temperature (°C) (3) | TOC (mg/L) (4) | Residual free chlorine (mg/L) (5) |
|---------------------------|-------------------|----------------------|-------------------|-----------------------------------|
| UWR-OPS | 7.52 ^a | 16.4 | 1.73 ^b | 0.98 |
| FWD-WTP | 8.15 ^a | 17.9 ^a | 1.87 ^b | 1.73 |
| RRA-A | 7.4 ^b | 25.0 ^b | 0.55 ^b | 3.9 |
| SLTP-A | 3.55 ^b | 25.0 ^b | 3.55 ^b | 10.0 |
| RRA-B | 7.42 ^b | 22.2 ^a | 0.56 ^b | 0.31 |
| SLTP-A | 8.85 ^a | 21.9 ^a | 3.55 ^b | 0.49 |
| 50/50 ASLW-B | 7.92 ^a | 22.1 ^a | 2.05 ^b | 0.40 |
| BWD-WWTP | 8.05 ^a | 17.4 ^a | 0.84 ^b | 0.72 |
| PES-3/23/94 | 7.8 | 14 | — | 0.6 |
| PES-6/8/94 | 8.00 | 16 | — | 0.62 |
| PES-6/16/94 | 7.80 | 16 | — | 0.67 |

^aMeasured in field during sampling study.

^bEPA laboratory study.

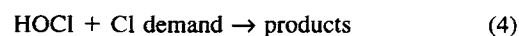
roform data were collected for NMWD-SLTP and the Bellingham system. In most cases TTHM samples were collected from a clear well slightly removed in time from the point of chlorination. Therefore, by the time the sample was taken, a small amount of TTHM had already formed. This anomaly was compensated for in the TTHM models. In several cases the variation in analytical results was so great that the data were virtually meaningless. The location and the nature of the water from each utility used in this analysis are described in Table 1.

MODEL DEVELOPMENT

Chlorine dissolved in water yields



HOCl generally reacts with the various components that make up chlorine demand as follows:



In (4), if the balanced reaction equation is represented by



where A and B = reacting substances; and P = product of the reaction, then the rate of reaction is given by

$$\frac{dC_A}{dt} = -k_A C_A C_B \text{ or } \frac{dC_B}{dt} = -k_B C_A C_B \text{ or } \frac{dC_P}{dt} = k_P C_A C_B \quad (6)$$

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

Equation for Chlorine Decay

Since both C_A and C_B change with time, to integrate the differential equation we must write a relation connecting them. 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

$$C_A = C_{A_0} - x \quad C_B = C_{B_0} - \frac{bx}{a} \quad (7)$$

$$dC_A = -dx = \frac{a}{b} dC_B \quad (8)$$

Substitution into (6) produces

$$-k_A(C_{A_0} - x)(C_{B_0} - bx/a) \quad (9)$$

Rearranging (9) yields

$$\frac{dC_A}{(C_{A_0} - x)(C_{B_0} - bx/a)} = k_A dt \quad (10)$$

Integrating (10) yields

$$\ln \frac{1 - x/C_{A_0}}{1 - bx/aC_{B_0}} = \left(\frac{bC_{A_0}}{a} - C_{B_0} \right) k_A \quad (11)$$

Let

$$r = \left(\frac{bC_{A_0}}{a} - C_{B_0} \right) \quad (12)$$

and

$$u = rk_A \quad (13)$$

Then

$$\frac{1 - x/C_{A_0}}{1 - bx/aC_{B_0}} = e^{-u} \quad (14)$$

If we let

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

then

$$C_A = \left(\frac{a}{b} C_{B_0} - C_{A_0} \right) / \left(\frac{aC_{B_0}}{bC_{A_0}} e^{-u} - 1 \right) \quad (16)$$

or

$$C_A = \left(C_{A_0} - \frac{a}{b} C_{B_0} \right) / \left(1 - \frac{aC_{B_0}}{bC_{A_0}} e^{-u} \right) \quad (17)$$

If we let

$$K = C_{A_0} - \frac{a}{b} C_{B_0} \quad (18)$$

and

$$R = \frac{aC_{B_0}}{bC_{A_0}} \quad (19)$$

then (18) can be rewritten as follows:

$$C_A = \frac{K}{1 - Re^{-u}} \quad (20)$$

Eq. (20) will be applied to the systems described in Table 1. In (20), C_A is the concentration of free chlorine. Rewriting (20) yields

$$Cl(t) = \frac{K}{1 - Re^{-u}} \quad (21)$$

where $Cl(t)$ = chlorine concentration in mg/L at time t ; and t = reaction time in minutes. Parameters to be estimated are R (dimensionless), K (mg/l), and u (min^{-1}).

TTHM Formation Equation

Based on (5), a TTHM formation equation was developed. Using (6) and eliminating time as a variable yields

$$\frac{dC_p}{dC_A} = -T \quad (22)$$

where

$$T = \frac{k_p}{k_A} \quad (23)$$

If we let

$$C_p = C_A y \quad (24)$$

then

$$C_A \frac{dy}{dC_A} + y = -T \quad (25)$$

We can assume that

$$C_A = C_{A_0}, \text{ at } y = 0$$

Therefore

$$C_p = T(C_{A_0} - C_A) \quad (26)$$

If we let

$$C_p = \text{TTHM} \quad (27)$$

where TTHM = total trihalomethanes; and C_A = chlorine residual (mg/L).

Then

$$\text{TTHM} = T \left\{ C_{A_0} - \left[\frac{C_{A_0}(1 - R)}{1 - Re^{-u}} \right] \right\} \quad (28)$$

where T = dimensionless parameter; C_{A_0} = initial chlorine residual (mg/L); and R , u = parameters from the chlorine decay equation. Eq. (28) demonstrates that using second-order kinetics TTHM formation can be characterized as a function of chlorine demand.

As mentioned earlier, in several cases samples were taken from a clear well or at some point after initial chlorination and therefore a small amount of TTHM had already formed by the time the sample was taken. Therefore, (28) was modified to

$$\text{TTHM} = T \left\{ C_{A_0} - \left[\frac{C_{A_0}(1 - R)}{1 - Re^{-u}} \right] \right\} + M \quad (29)$$

where M = estimated value of TTHM at time zero.

Parameter Estimation for Chlorine Decay Equation

The use of (21) provides results equivalent to or better than the models used in Vasconcelos et al.'s (1996) study.

Reformulating (21) yields

$$Cl(t) = \frac{Cl_0(1 - R)}{1 - Re^{-u}} \quad (30)$$

assuming that

$$Cl(t) = Cl_0, \text{ at } t = 0$$

where Cl_0 = initial value of free chlorine (mg/L).

Eqs. (12)–(19) show that if $u > 0$, then $R < 1$ and $K > 0$. If $u < 0$, then $R > 1$ and $K < 0$.

The modified Gauss-Newton method was used to compute the least squares estimates of the two nonlinear models (Hartly

TABLE 2. Parameter Estimates for First- and Second-Order Equations

| Site (1) | First-Order | | Second-Order | | | |
|--------------|-------------|--------------|--------------|------------|--------------------|--------------|
| | K (2) | r^2 (3) | K (4) | R (5) | U (6) | R^2 (7) |
| UWR-OPS | 0.0097 | 0.944 | 0.065 | 0.933 | 9×10^{-4} | 0.960 |
| FWD-WTP | 0.048 | 0.834 | 1.0002 | 0.4207 | 0.12 | 0.961 |
| RRA-A | 0.0022 | 0.158 | 3.594 | 0.078 | 0.1557 | 0.879 |
| STLP-A | 0.01455 | 0.957 | 9.854 | 0.9027 | 0.00257 | 0.989 |
| RRA-B | 0.044 | 0.707 | 0.099 | 0.677 | 0.038 | 0.812 |
| STLP-B | 0.73 | 0.982 | -0.33 | 1.67 | -0.42 | 0.989 |
| 50/50 ASLW-B | 0.45 | 0.948 | -0.02 | 1.05 | -0.04 | 0.990 |
| BWD-WWTP | 0.035 | 0.788 | 0.266 | 0.631 | 0.051 | 0.987 |
| PES-3/23/94 | 0.001 | 0.931 | -0.01 | 1.02 | -0.0025 | 0.958 |
| PES-6/8/94 | 0.07 | 0.729 | 0.22 | 0.65 | 0.08 | 0.907 |
| PES-6/16/94 | 0.06 | 0.778 | 0.23 | 0.66 | 0.06 | 0.948 |

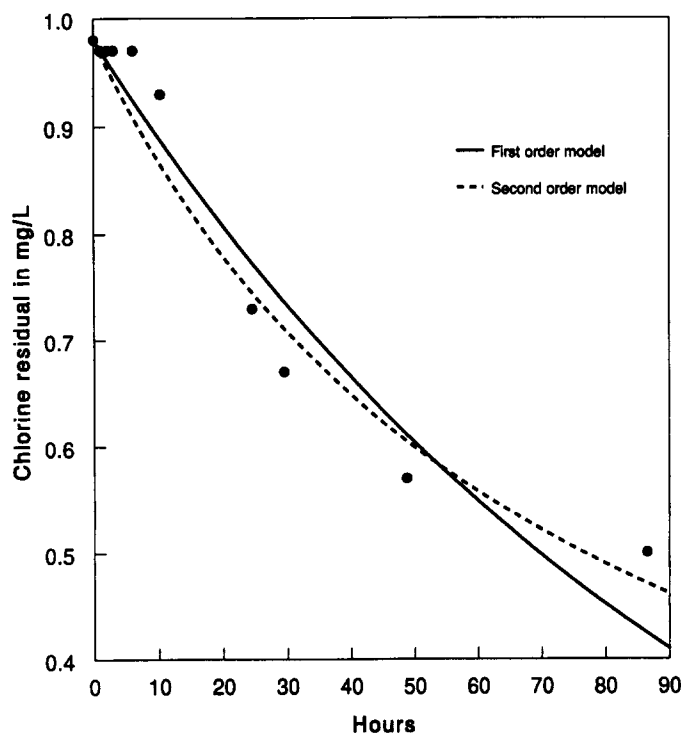


FIG. 1. Chlorine Demand in mg/L versus Time in Hours at United Water Resources: Oberlin Pump Station (UWR-OPS)

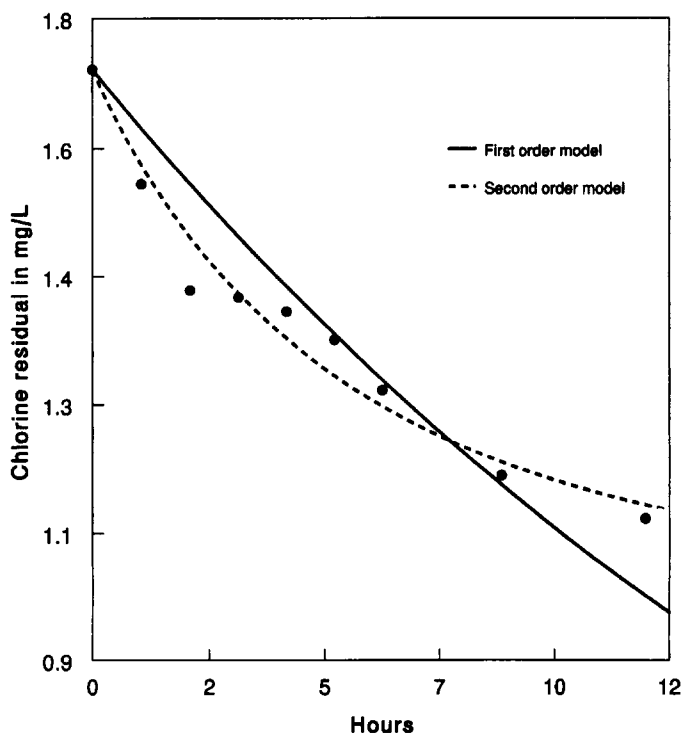


FIG. 2. Chlorine Demand in mg/L versus Time in Hours for City of Fairfield Water Department: Waterman Treatment Plant (FWD-WTP)

1961). This method uses the first-order Taylor series expansion for the nonlinear functions of the independent variable (time) and the parameters. This method and the SAS procedure NLIN are used to estimate the model parameters. The procedure regresses the residuals (observed versus predicted) against the partial derivatives of the model with respect to the parameters until the estimates converge.

Parameters were estimated for second-order equation (30)

and first-order equation (2) for the cases contained in Table 1. The estimates for these parameters are shown in Table 2.

In all of the cases examined the r^2 values were higher in the second-order model than in the first-order model. Figs. 1–11 compare the first-order fit to the second-order fit of the data in Table 1. As Table 2 and Figs. 1–11 show, the second-order equation provides the best fit for all of the data sets.

Vasconcelos et al. (1996) estimated parameters for the various equation forms mentioned earlier. Table 3 compares Vas-

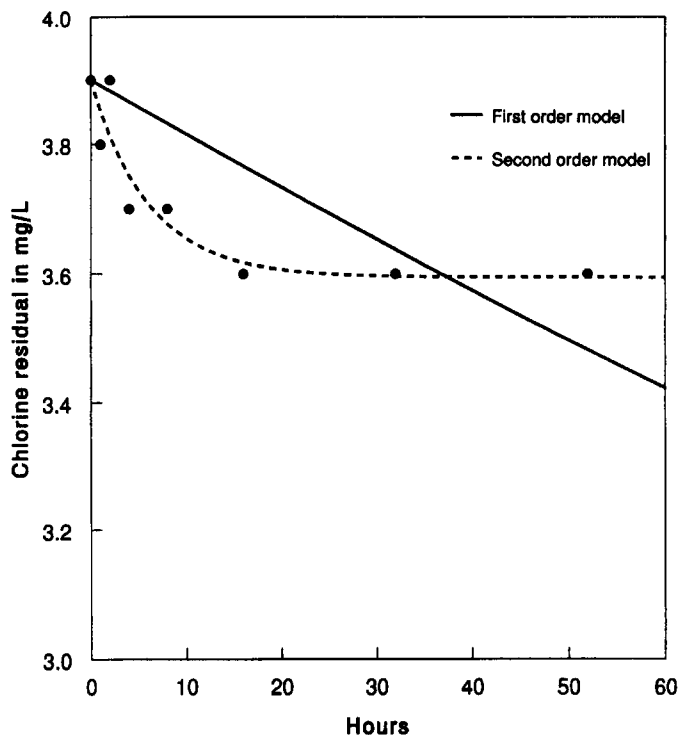


FIG. 3. Chlorine Demand in mg/L versus Time in Hours for North Marin Water District: Russian River Aqueduct (RRA-A)

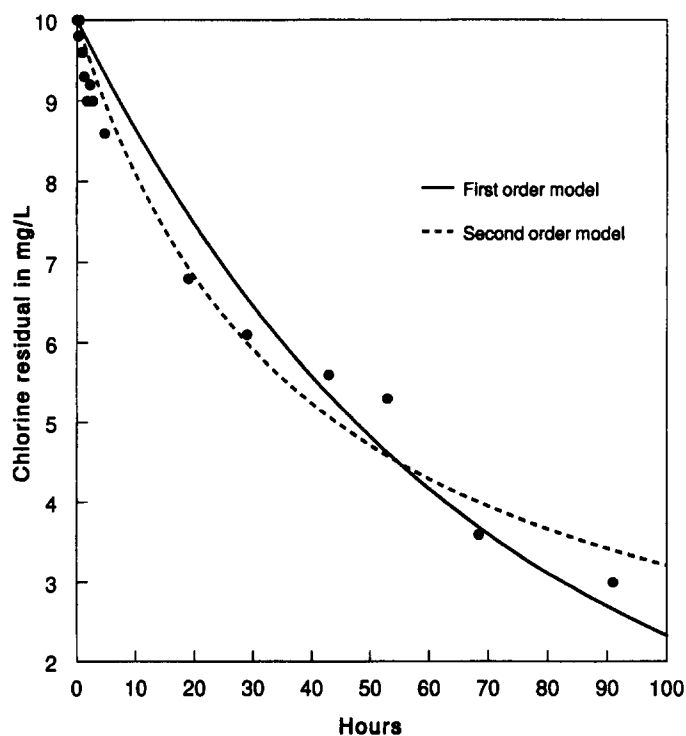


FIG. 4. Chlorine Demand in mg/L versus Time in Hours for North Marin Water District: Stafford Lake Treatment Plant (SLTP-A)

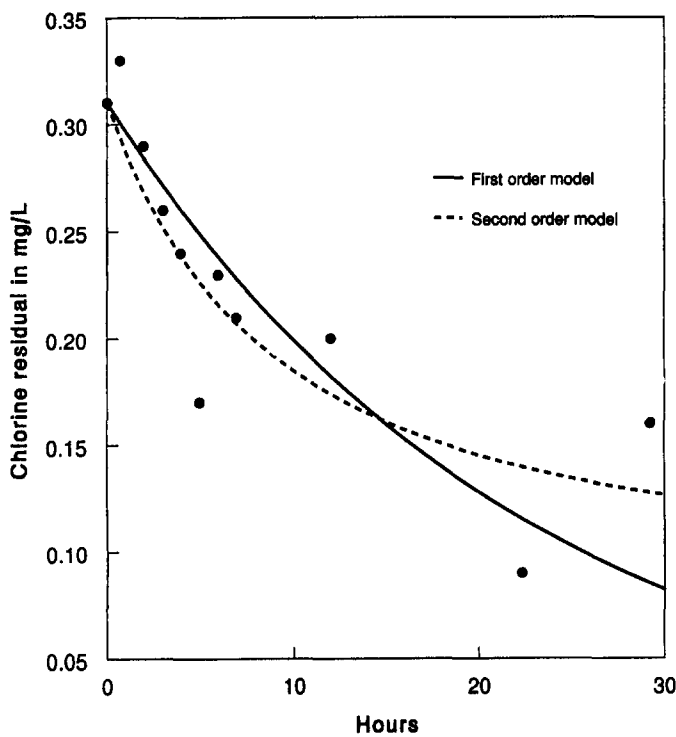


FIG. 5. Chlorine Demand in mg/L versus Time in Hours for North Marin Water District: Russian River Aqueduct (RRA-B)

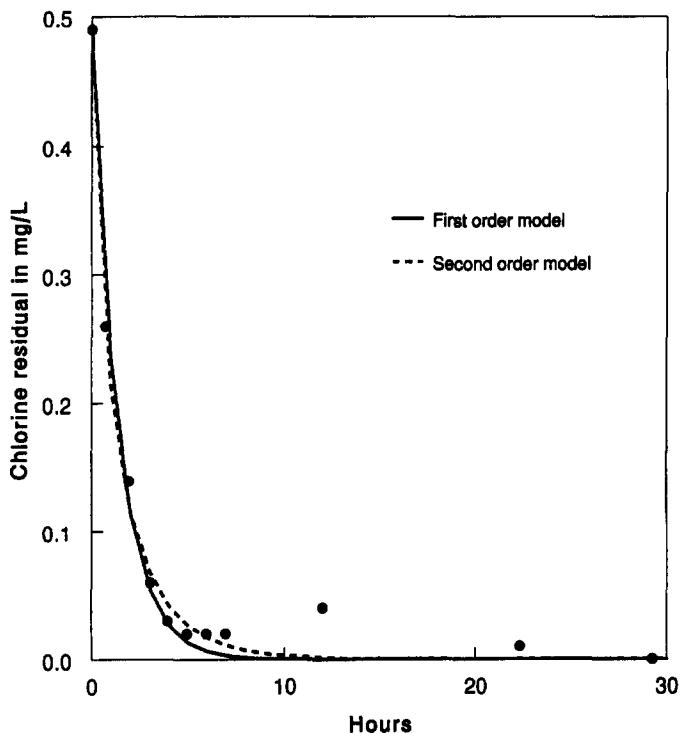


FIG. 6. Chlorine Demand in mg/L versus Time in Hours for North Marin Water District: Stafford Lake Treatment Plant (SLTP-B)

concelos et al.'s (1996) results with the analysis presented in this paper. In some cases the r^2 values of the first-order decay model obtained in this study were lower than those reported by Vasconcelos et al. (1996). In those cases the r^2 values are shown in parentheses in column 2. The second-order model developed in this study (column 6) was as good as or better than the models analyzed in Vasconcelos et al.'s (1996) study.

If we assume that C_B , the second reactant in (5) is TOC, then based on (6)–(21) we would expect a value of $R > 1$ to

result in a very rapid decline in chlorine residual. Figs. 3–7 for the NMWD illustrate this effect. The RRA is a high-quality, low-TOC source water relative to SLTP water, which is of poor quality with a high TOC. The STLP water experiences a much more rapid loss of chlorine residual than does RRA water.

Table 3 shows that the second-order equation is comparable to both the n th order and parallel-order equations that were

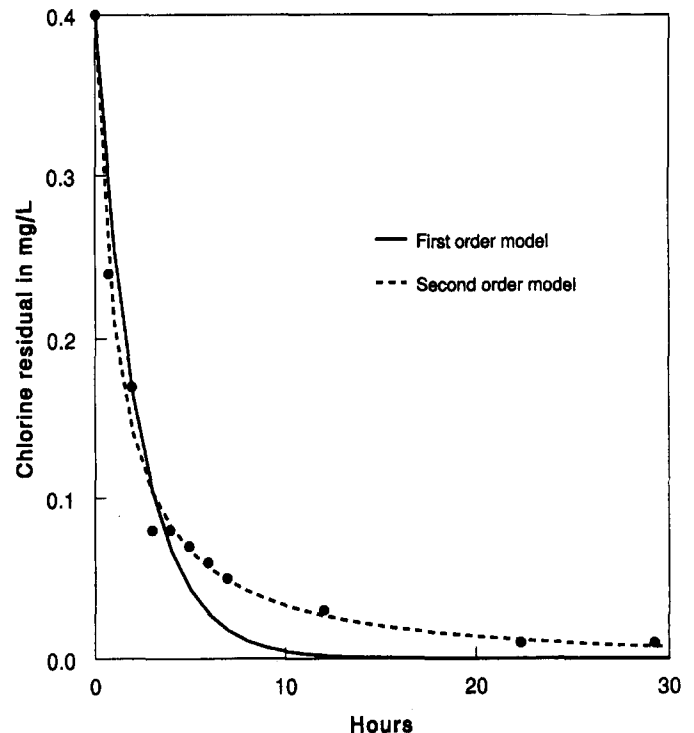


FIG. 7. Chlorine Demand in mg/L versus Time in Hours for North Marin Water District: 50/50 Blend of Aqueduct and Stafford Lake Water (50/50 ASLW-B)

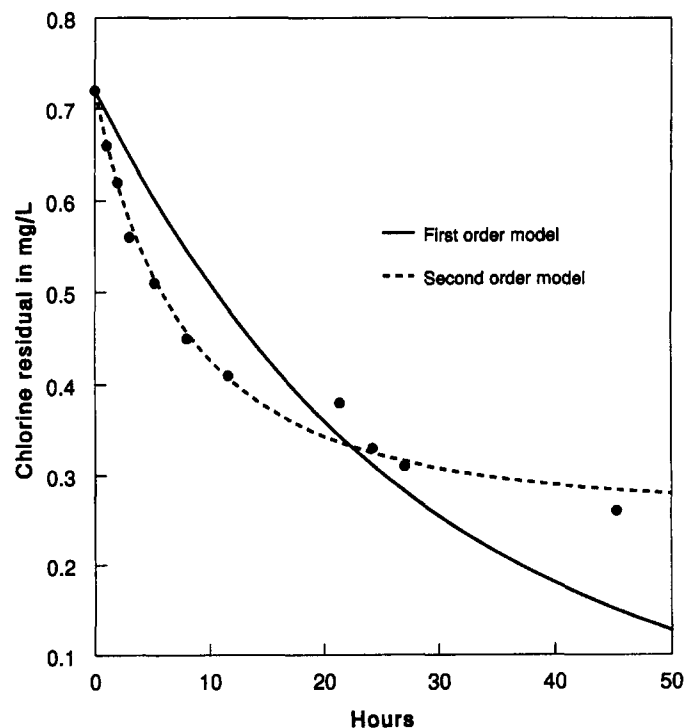


FIG. 8. Chlorine Demand in mg/L versus Time in Hours for City of Bellingham Water Department: Welcome Water Treatment Plant (BWD-WWTP)

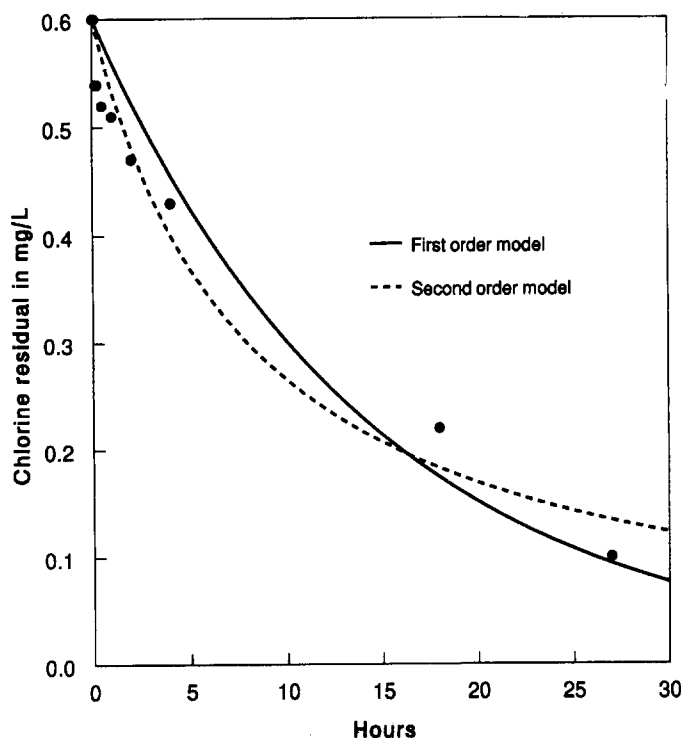


FIG. 9. Chlorine Demand in mg/L versus Time in Hours for Parisienne des Eaux System, 3/23/94 (Pes-3/23/94)

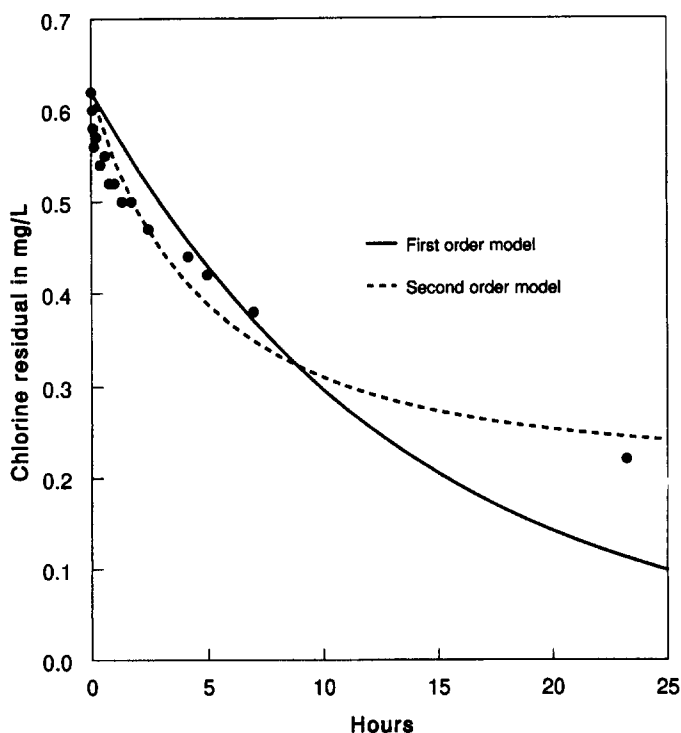


FIG. 10. Chlorine Decay in mg/L versus Time in Hours for Parisienne des Eaux System, 6/8/94 (PES-6/8/94)

found to be best in Vasconcelos et al.'s (1996) study, and the second-order equation is superior to five out of six of the first-order fits.

Estimation of Parameters for Chlorine Decay and TTHM Formation

To illustrate that the models developed here can be used to characterize TTHM formation as a function of chlorine demand, the parameters in (21) and (29) were estimated using

data from the Vasconcelos et al. (1996) study and from the Clark et al. (1994) study. Consistent and reliable data were available for FWD-WTP, SLTP, RRA-A, RRA-B, 50/50 ASLW-B, and BWD-WWTP. The parameters for (21) and (29) are in Table 4.

Figs. 12–17 display the results of estimating the parameters in (21) and (29) simultaneously.

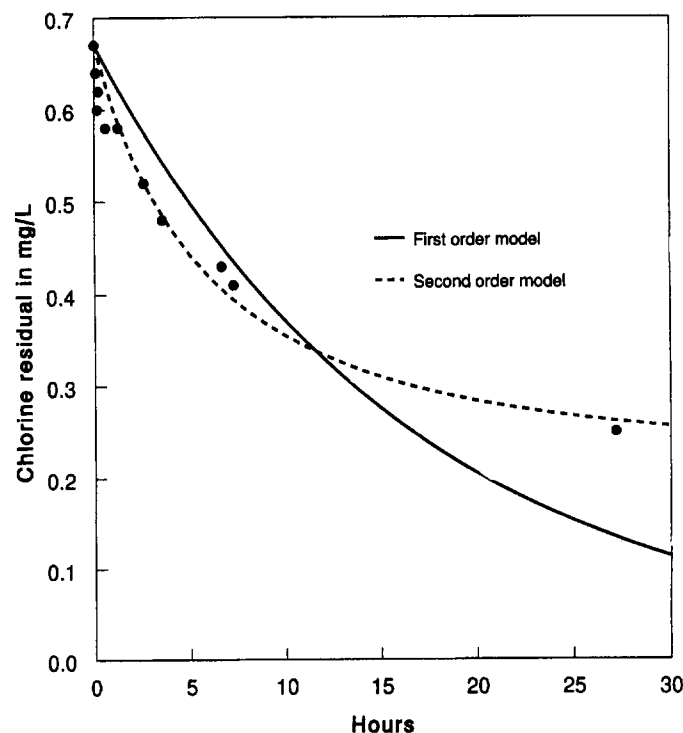


FIG. 11. Chlorine Demand in mg/L versus Time in Hours for Parisienne des Eaux System, 6/16/94 (PES-6/16/94)

TABLE 3. Comparison of Various Curve-Fitting Approaches

| Site (1) | First order (2) | <i>n</i> th order (3) | Limited first-order (4) | Parallel first-order (5) | Second- order (6) |
|--------------|-----------------------|-----------------------------|-------------------------------|--------------------------------|-------------------------|
| UWR-OPS | 0.994 | 0.995 | 0.960 | — | 0.960 |
| FWD-WTP | 0.834 | 0.966 | 0.948 | 0.978 | 0.961 |
| RRA-B | 0.707 (0.839) | 0.827 | 0.824 | 0.808 | 0.812 |
| STLP-B | 0.982 (0.990) | 0.995 | 0.993 | 0.986 | 0.989 |
| 50/50 ASLW-B | 0.948 (0.946) | 0.989 | 0.974 | 0.986 | 0.990 |
| BWD-WWTP | 0.788 (0.931) | 0.991 | 0.973 | 0.993 | 0.987 |

Note: Numbers in parentheses = r^2 from the Vasconcelos study.

TABLE 4. Parameters for Chlorine Decay and TTHM Formation Models

| Site (1) | Chlorine Decay | | | TTHM Formation | |
|--------------|---------------------------|---------------------------|---|---------------------------|-----------------|
| | <i>K</i> (mg/L) (2) | <i>R</i> (mg/L) (3) | <i>u</i> (min ⁻¹) (4) | <i>M</i> (μg/L) (5) | <i>T</i> (6) |
| SLTP-A | 7.03 | 0.2974 | 0.252 | — | 56.43 |
| RRA-A | 3.58 | 0.0828 | 0.072 | — | 72.52 |
| FWD-WTP | 1.298 | 0.2500 | 0.440 | 10.0 | 41.29 |
| RRA-B | 0.160 | 0.4829 | 0.293 | — | 126.73 |
| 50/50 ASLW-B | 0.028 | 0.9299 | 0.193 | — | 188.60 |
| BWD-WWTP | 0.160 | 0.7773 | 0.017 | 17.0 | 36.27 |

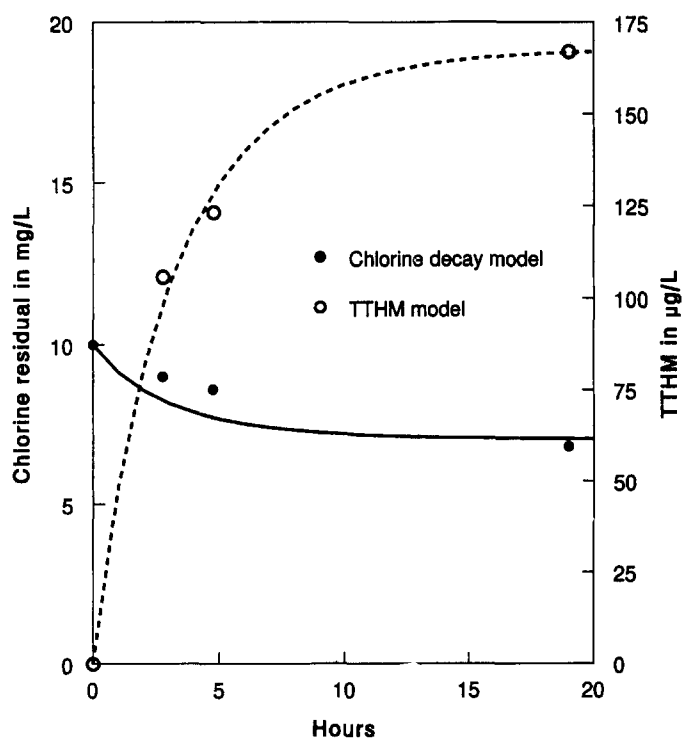


FIG. 12. TTHM Formation ($\mu\text{g/L}$) and Chlorine Demand (mg/L) versus Time in Hours for North Marin Water District: Stafford Lake Treatment Plant (SLTP-A)

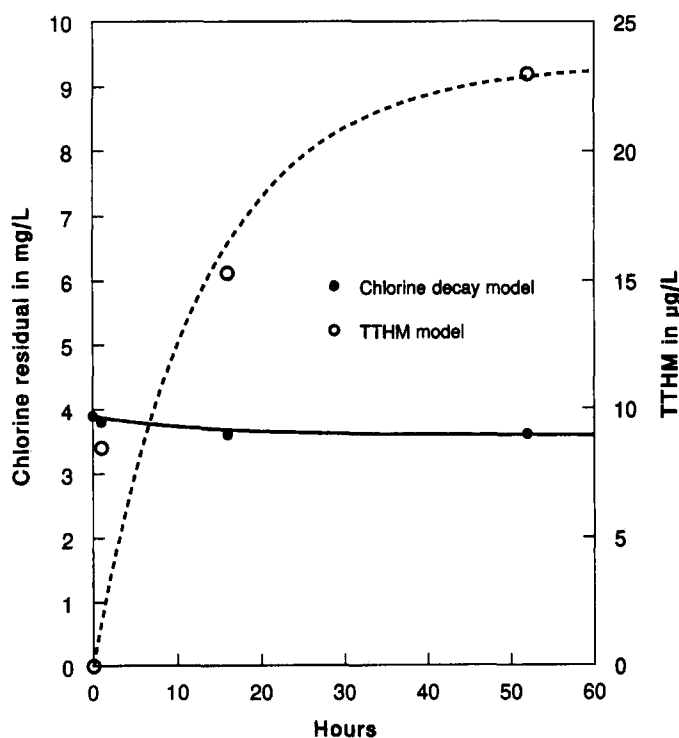


FIG. 13. TTHM Formation ($\mu\text{g/L}$) and Chlorine Demand (mg/L) versus Time in Hours for North Marin Water District: Russian River Aqueduct (RRA-A)

DISCUSSION

Most municipal water systems 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, use of a primary disinfectant is followed by use of another disinfectant. 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 trihalomethanes (THMs), by-products other than chloroform (e.g., bromodichloromethane), haloacetic acids (HAAs), haloacetonitriles, haloketones, and haloaldehydes. All of the disinfectants mentioned are reactive; ozone, chloramines, and

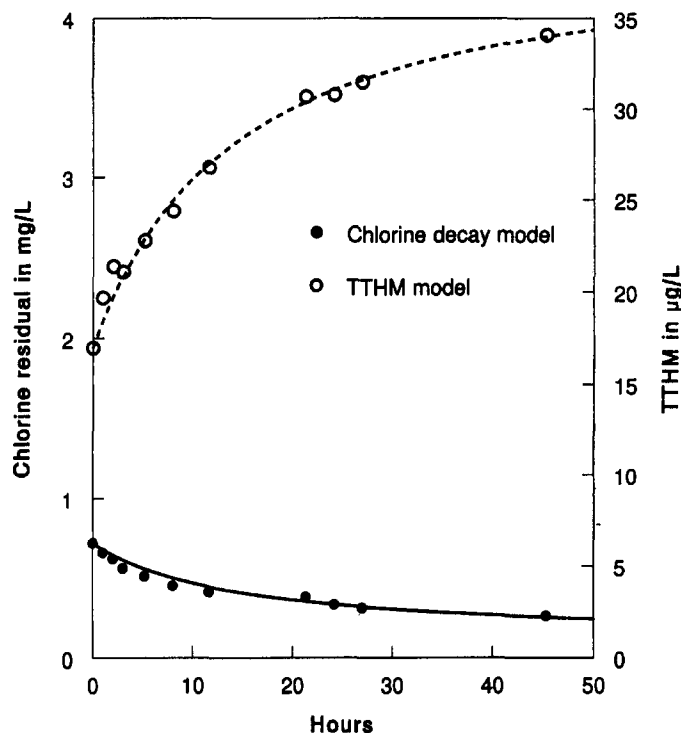


FIG. 14. TTHM Formation ($\mu\text{g/L}$) and Chlorine Demand (mg/L) versus Time in Hours for City of Bellingham Water District: Welcome Water Treatment Plant (BWD-WWTP)

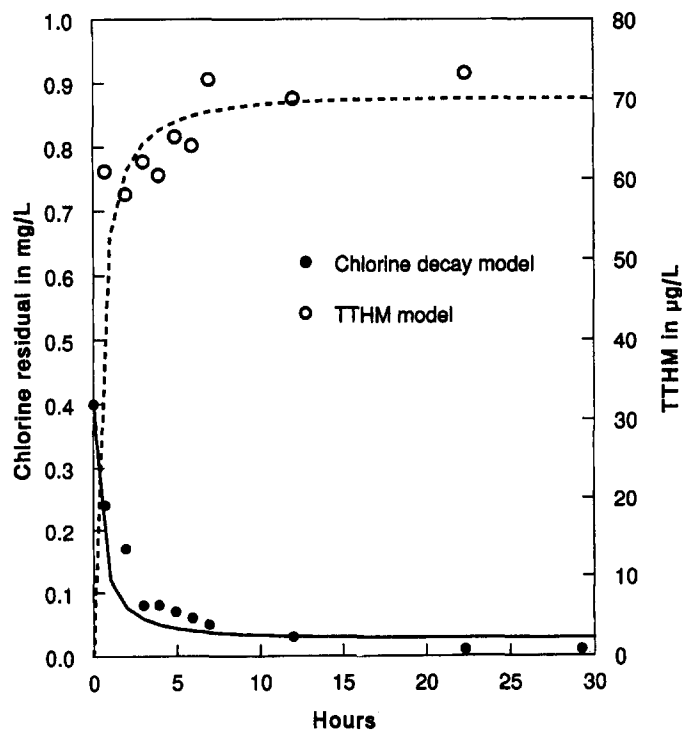


FIG. 15. TTHM Formation ($\mu\text{g/L}$) and Chlorine Demand (mg/L) versus Time in Hours for North Marin Water District: 50/50 Blend of Aqueduct and Stafford Lake Water (50/50 ASLW-B)

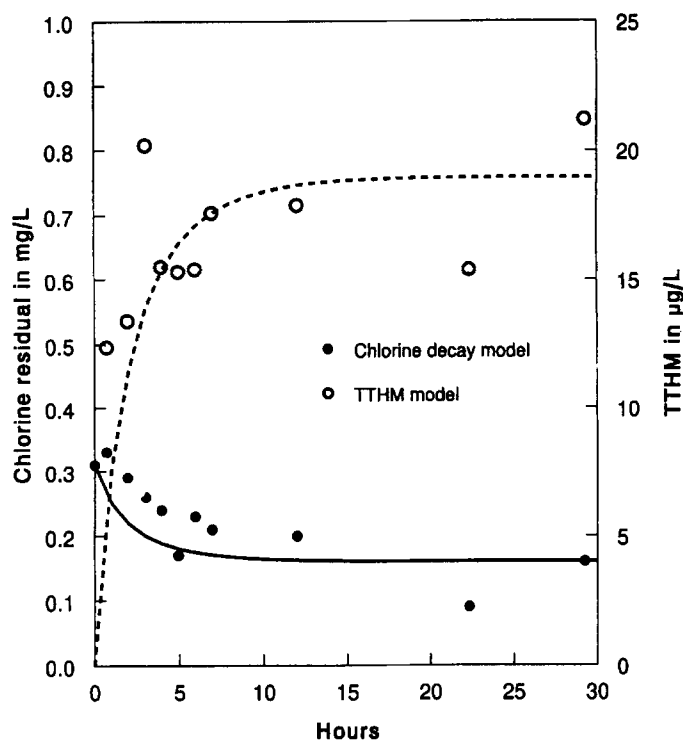


FIG. 16. TTHM Formation ($\mu\text{g/L}$) and Chlorine Demand (mg/L) versus Time in Hours for North Marin Water District: Russian River Aqueduct (RRA-B)

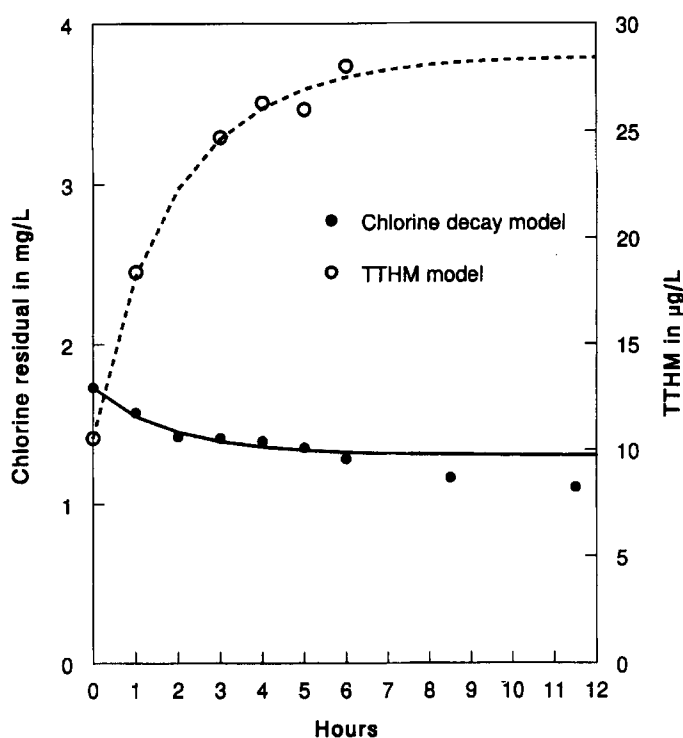


FIG. 17. TTHM Formation ($\mu\text{g/L}$) and Chlorine Demand (mg/L) versus Time in Hours for City of Fairfield Water Department: Waterman Treatment Plant (FWD-WTP)

chlorine dioxide result in both organic and inorganic by-products. More than 500 DBPs have been identified in tap water (Clark et al. 1996).

Chlorine is the most widely used disinfectant in the United States, and research has therefore focused on exposure to chlorinated drinking water. A key yet complex issue is balancing the microbial and DBP risks associated with the disinfection of drinking water.

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 byproduct formation during distribution. Two- and fourfold differences can 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 over the course of a year.

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. Therefore, there is a great deal of interest in understanding the factors that affect the formation of disinfection by-products during the distribution of drinking water.

This paper presents a model that links the formation of trihalomethanes to the consumption of chlorine and the maintenance of chlorine residuals in drinking water. The model should help to provide a quantitative framework for assessing the tradeoffs between the microbial and DBP risks associated with the disinfection of drinking water.

Data used in developing this model were collected under laboratory conditions to eliminate the site-specific effects that individual distribution systems may have on the loss of chlorine residuals. These distribution system effects are well documented in papers by Rossman et al. (1994) and Clark et al. (1995); the equations presented in these two papers can be used in conjunction with the model developed here to simulate the effect of chlorine residual loss in a specific distribution network.

SUMMARY AND CONCLUSIONS

Rules and regulations established under the Safe Drinking Water Act and its 1986 and 1996 amendments have emphasized the importance of maintaining disinfectant residuals in drinking water distribution systems. There is also concern over 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 in water. Chlorine demand in distribution systems is generally assumed to be composed of a wall decay component and a bulk decay component, which are usually assumed to be first-order in nature. Vasconcelos et al. (1996) have shown that the n th-order and parallel-order decay equations best describe the chlorine decay in the study described here. This paper shows that a second-order kinetic model provides an equivalent fit.

ACKNOWLEDGMENTS

The writer would like to gratefully acknowledge the assistance of Mano Sivaganesan (statistician, Lockheed Environmental Systems Technologies Co.), Jean Lillie, Toni Frey, Sandra Taylor, and Steven Waltrip of the WSWRD for their assistance in preparing this paper.

APPENDIX I. REFERENCES

- Amy, G. L., Chadik, P. A., and Chowdhury, Z. K. (1987). "Developing models for predicting trihalomethane formation potential and kinetics." *J. AWWA*, 79(7), 89–97.
- Clark, R. M., Goodrich, J. A., and Wymer, L. J. (1993). "Effect of the distribution system on drinking water quality." *J. Water Supply Res. and Technol. AQUA*, 42(1), 30–38.
- Clark, R. M., Smalley, G., Goodrich, J. A., Tull, R., Rossman, L. A., Vasconcelos, J. J., and Boulos, P. F. (1994). "Managing water quality in distribution systems: Simulating TTHM and chlorine residual propagation." *J. Water Supply Res. and Technol. AQUA*, 43(4), 182–191.
- Clark, R. M., Rossman, L., and Wymer, L. (1995). "Modeling distribution system water quality: Regulatory implications." *J. Water Resour. Plng. and Mgmt.*, ASCE, 121(6), 423–428.
- Clark, R. M., Pourmoghaddas, H., Wymer, L. G., and Dressman, R. C. (1996). "Modeling the kinetics of chlorination by-product formation:

- The effects of bromide." *J. Water Supply Res. and Technol. AQUA*, 45(1), 1–8.
- Haas, C. N., and Karra, S. B. (1984). "Kinetics of wastewater chlorine demand exertion." *J. WPCF*, 56(2), 170–173.
- Hartly, H. O. (1961). "The modified Gauss-Newton method for the fitting of nonlinear regression functions by least squares." *Technometrics*, 3, 269–280.
- Rossman, L. A., Clark, R. M., and Grayman, W. M. (1994). "Modeling chlorine residuals in drinking water distribution systems." *J. Envir. Engrg.*, ASCE, 120(7), 803–820.
- Vasconcelos, J. J., Boulous, P. F., Grayman, W. M., Kiene, L., Wable, O., Biswas, P., Bhari, A., Rossman, L. A., Clark, R. M., and Goodrich, J. A. (1996). *Characterization and modeling of chlorine decay in distribution systems*. AWWA Research Foundation, Denver, Colo.

APPENDIX II. NOTATION

The following symbols are used in this paper:

- | | |
|---|---|
| A = reacting substance; | C_o = initial concentration of chlorine in the bulk phase; |
| a = coefficient of reacting substance A ; | $C(t)$ = chlorine decay in the bulk phase at time t ; |
| B = reacting substance; | dc = rate of change of chlorine decay in the bulk phase; |
| b = coefficient of reacting substance B ; | dc_A = rate of change for the concentration of substance A ; |
| c = chlorine decay in the bulk phase; | dc_B = rate of change for the concentration of substance B ; |
| C_A = concentration of reacting substance A ; | dc_P = rate of change for the concentration of the products; |
| C_{ao} = initial concentration of substance A ; | dt = rate of change in time; |
| C_B = concentration of reacting substance B ; | e = base for natural logarithm; |
| C_{bo} = initial concentration of substance B ; | HCl = hydrochloric acid; |
| $C(ct)$ = concentration of chlorine at any time t ; | HOCl = hypochlorous acid; |
| c/demand = chlorine demanding compounds; | H_2O = water; |
| Cl_o = concentration of chlorine at time zero; | k = first-order decay constant, which is a function of initial concentrations of substances A and B and their coefficients; |
| Cl_2 = chlorine; | 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; |
| | 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 = constant in TTHM formation equations; |
| | t = time; |
| | t = ratio of the rate of change in C_A to the rate of change in C_B ; |
| | TTHM = total trihalomethane concentration; |
| | u = reaction rate constant; |
| | x = concentration of A that has reacted; and |
| | Y = variable indicating ratio of the concentration of the produce to substance A . |