

# Modeling daily variation of trihalomethane compounds in drinking water system, Houston, Texas

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## Abstract

Total trihalomethanes (TTHM) concentrations vary widely and periodically between 70 and 130 ppb. Data from the National Environmental Services Laboratory, Houston, Texas indicate that pH and free residual chlorine contribute minimally to the wide variability of TTHM levels. Temperature variation in drinking fluctuates from 11 to 27 °C. The objective of this research is to formulate a model that delineates more clearly the daily variations of the most prevalent volatile trihalomethane by-products: chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBr<sub>2</sub>Cl), and bromoform (CHBr<sub>3</sub>) levels from drinking water. This model simulates the daily fluctuation of THM at a single location and at any time during the day as a function of the water temperature and the average concentration of TTHM, which can be estimated. The hypothesis of this study is that observed daily fluctuations of TTHM, CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub> are periodic. This hypothesis is tested using autocorrelation functions and it is shown that for the series of pH the correlation coefficient is maximal at zero lags, rapidly decreases to zero, and increases again between 4- and 6-h period. Such pattern suggests random fluctuation unrelated to time. However, the series of free residual chlorine, temperature, TTHM, CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub> suggest a different pattern. The correlation coefficient increases when the time-shift approaches 24 h. These repetitions in fluctuation of content over a 24-h period are statistically significant. The model formulated in this study provides insights in TTHM variation and is a necessary tool to reduce the error when estimating potential risk from exposure to trihalomethane compounds in drinking water system. In general, calculation of potential risk by using a value measured early morning or late afternoon concentrations were found minimal lead to an underestimation of the population risk.

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**Keywords:** Water temperature; Top water; Trihalomethane level; Distribution system; Autocorrelation; Stagnation; Flashing

## 1. Introduction

### 1.1. Temperature impact

A temperature effect on the THM formation potential has been noted by episodic observations from field studies. For instance, Rook [9] observes that consumption of chlorine increases when temperature increases and more THM are formed, while Symons et al. [13] suggest that differences in temperature would affect THMFP. Fram [2] states that with more volatile THM, more species are produced at higher temperature and Oliver [7] affirms that low temperature aids in the retention

of a chlorine residual by reducing the rates of reaction leading to hypochlorous acid removal. In general, the rates of chemical reactions decrease with decreasing temperature. The relative concentrations of reactants and products in chemical equilibrium can also change with temperature. The magnitude of this change depends on the Gibbs free energy change of the reaction in question. Rodriguez and Serodes [8] state that increasing the temperature will also increase the vapor pressure of trace THM formation. Stevens et al. [12] demonstrate that the rate of formation of chloroform in raw water treated with a chlorine dose of 10 mg/L increased threefold between 3 and 25 °C. In a survey of organics in Ontario drinking water, Stevens et al. [11] conclude that water temperature was perhaps the single most important factor influencing seasonal variation in TTHM concentrations.

Moreover, many researchers have studied the chemical reaction of NOM that is a non-living component, which are a

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heterogeneous mixture composed largely of products resulting from microbial and chemical transformations of organic debris with chlorine using different NOM components based on the origin and pathway taken by the surface water, vegetation, soil type, and climate. These researchers conclude that the hydrolysis is a rate-limiting step for the THM formation potential because the increase of water temperature changes the dissociation of  $H^+$  and  $OH^-$  making the water either more acidic or alkaline and this phenomenon act as catalyst for hydrolysis reaction.

It has been suggested by the literature that concentration variability of THM compounds in tap water may play a larger role than behavioral characteristics (for example, showering duration) in determining individual exposure. This study will help to determine the pattern of variability in disinfection by-products at a specific point in the distribution system and within 24-h period. The first hypothesis of this study is that the fluctuation of TTHM and its components is periodic. The second hypothesis test whether the periodic model formulated for this study describes the observed variation of measured TTHM concentrations and concentrations of subject TTHM components.

## 2. Materials and methods

### 2.1. Texas database

The database used in this study was obtained from the National Environmental Services Laboratory of Houston, Texas. This data set was collected in 1980 at a location 15 km from treatment plant from constantly flowing tap water at a medical center. This water has been found to contain comparatively high concentrations of THM. Samples were drawn during the weeks of November–December 1980 at 10 a.m., 2 p.m., 6 p.m., 10 p.m., 2 a.m., and 6 a.m. This database will be used to investigate and model the daily change of TTHM as a function of time. This site was chosen because: water distributed within the Houston Medical Center is of surface origin, derived from the San Jacinto River via Lake Houston. The water had been found to contain comparatively high concentrations of THM. San Jacinto River water is distributed within the city of Houston from a single treatment plant to approximately 50% of Houston residents. Additionally, building security and other facilities allowed investigators to remain on the site for the duration of the sampling, including nocturnal sampling hours.  $CHCl_3$ ,  $CHBr_3$ ,  $CHCl_2Br$ ,  $CHClBr_2$ , water temperature, pH and residual chlorine of drinking water were measured every 4 h for 7 weeks by Smith et al. [10].

THM concentrations were measured every 4 h for 49 days at the site of the University of Texas Health Science Center. While this is not a residential environment, the daily THM level variation should not be different as a function of the sampling site type.

### 2.2. Sub-model: daily variation of trihalomethane level

A sub-model is formulated to simulate the daily fluctuation of THM at a single location. The two important factors that affect this daily fluctuation of THM in the distribution system are: (1) stagnation and flashing periods and (2) temperature. In

order to identify the plant stagnation and flashing system effect on the daily THM variation a time series-forecasting model is formulated as is explained below.

Box–Jenkins methods require at least 40 or 50 equally spaced periods of data. The data input must be adjusted in the following stepwise manner, Farnum and Stanton [1].

*Step one.* In order to detect a potential of 24-h cycle, weekly trend, or any other systematic feature and distinguish it from purely random fluctuations a lagged autocorrelation is used [3–6].

Autocorrelation is the correlation between observations of a time series separated by  $k$  time units. The plot of autocorrelation is called the autocorrelation function or acf.

Once we prove that the system is periodic, a harmonic function model is applied to describe the variation of THM concentration in the distribution system as a function of flushing and stagnation processes.

A wave type model using a harmonic equation and an iteration method fits a given dataset as described below:

$$Y = Y_0 + a \sin \left[ \frac{2\pi t}{P} \right] \quad (1)$$

where  $Y$  is the THM level at any time of the day;  $Y_0$  the average value of THM during the 24-h defined cycle or period;  $a$  the maximum variation above and below the average, also called amplitude of the periodic function;  $P$  is the parameter representing the period of the function defined by the program and  $t$  is the time of the day.

*Step two.* Up to 600 iterations are used to fit this type of equations. The iterative approach models every cycle (24-h period) separately. Therefore, we have 49 different sets of equations (7 cycles every week for 7 weeks). These 49 different equations have different amplitude value ( $a$ ), different  $Y_0$  and different parameter  $P$  [3]. The form is as follows:

$$Y_{ij} = Y_{0ij} + a_{ij} \sin \left[ \frac{2\pi t}{P_{ij}} \right] \quad (2)$$

where  $i$  is the day and  $j$  is the week.

*Third step,* the values of the parameter  $P$  and the variable  $a_{ij}$  from the iteration process output will be studied using iteration process. This process leads to 49 different regression equations, and 49 different sets of amplitude  $a_{ij}$  and  $P_{ij}$  values. Each equation is checked for adequacy using the following criteria:

- (1) The predicted residual error sum of squares (PRESS) gauges how well a regression model predicts new data. The smaller the PRESS statistic, the better the predictive ability of the model.
- (2) The power, or sensitivity, of a regression is the probability that the model correctly describes the relationship of the variables, if there is a relationship.
- (3) The mean square provides an estimate of the population variance.
- (4) The  $F$ -test statistic gauges the contribution of the independent variables in predicting the dependent variable.

Table 1  
Descriptive statistics of daily variation of TTHM in the distribution system: Thursday, Friday, Saturday, Sunday, Monday, Tuesday, and Wednesday

Variable	<i>N</i>	Mean	Median	TrMean	S.D.	S.E. mean
Thursday	7	97.43	93.00	97.43	12.58	4.76
Friday	7	97.29	95.00	97.29	11.64	4.40
Saturday	7	100.00	95.00	100.00	13.93	5.26
Sunday	7	94.41	94.20	94.41	8.07	3.05
Monday	7	98.46	94.20	98.46	10.88	4.11
Tuesday	7	99.14	96.00	99.14	9.10	3.44
Wednesday	7	97.79	96.00	97.79	10.78	4.07

Variable	Minimum	Maximum	$Q_1$	$Q_3$
Thursday	85.00	120.00	88.00	109.00
Friday	83.00	119.00	89.00	104.00
Saturday	84.00	122.00	89.00	115.00
Sunday	82.70	109.00	89.00	97.00
Monday	84.00	116.00	92.00	108.00
Tuesday	92.00	118.00	92.00	103.00
Wednesday	84.00	117.00	90.00	105.50

(5) The *P* value, or the probability of falsely rejecting the null hypothesis, or committing a Type I error, based on *F*-test statistics.

The modeling process described above will help estimate the THM concentrations at any time of the day at a specific location in the distribution system.

### 3. Results

Descriptive statistics of the collected data are shown for TTHM for a randomly selected week (second week of November 1980), see Table 1, and for temperature, see Table 2. Similar tables have been formulated for each subject THM compound (bromoform, chloroform, dibromochloromethane) and for every week.

Table 2  
Descriptive statistics of daily variation of water temperature in the distribution system: Thursday, Friday, Saturday, Sunday, Monday, Tuesday, and Wednesday

Variable	<i>N</i>	Mean	Median	TrMean	S.D.	S.E. mean
Thursday	7	23.43	25.00	23.43	4.39	1.66
Friday	7	25.714	26.000	25.714	1.799	0.680
Saturday	7	17.86	17.00	17.86	3.72	1.40
Sunday	7	14.29	14.00	14.29	5.06	1.91
Monday	7	19.71	20.00	19.71	5.77	2.18
Tuesday	7	21.00	21.00	21.00	3.37	1.27
Wednesday	7	18.00	19.00	18.00	3.56	1.35

Variable	Minimum	Maximum	$Q_1$	$Q_3$
Thursday	19.00	29.00	19.00	28.00
Friday	23.000	28.000	24.000	27.000
Saturday	14.00	25.00	15.00	20.00
Sunday	9.00	20.00	9.00	20.00
Monday	13.00	31.00	15.00	21.00
Tuesday	15.00	26.00	20.00	23.00
Wednesday	12.00	22.00	15.00	21.00

Fig. 1 shows the concentration of total trihalomethane (TTHM) in drinking water over one entire week from the study period, and displays the variation in concentration as a function of time during each day. It is apparent that there is a wide variation in TTHM from 70 ppb to nearly its double, 130 ppb, and there appears to be a periodic rise and fall in these concentrations. The lowest values were observed in the nocturnal hours, between 10 p.m. and 2 a.m.; the highest values were observed daily near 2 p.m. Rapid changes in concentrations were found to occur, by as much as 30–40 ppb within 4 h. The average concentration of total trihalomethane was 98 ppb, with the highest level observed on Saturday morning and the lowest on Tuesday evening.

The 24-h average concentrations ranged from 116 ppb on Saturday to 86 ppb on Monday. Concurrent measurements of pH and chlorine both show rather small fluctuations. Free residual chlorine ranged from non-detectable to trace quantities, while pH varied from 7.6 to 7.9, which demonstrates that pH and free residual chlorine contribute minimally to the wide variability seen in total trihalomethanes (see Fig. 2). Temperature variation in drinking water was measured and it was found to fluctuate from 11 to 27 °C. Temperature generally peaked between 10 a.m. and 2 p.m., while lower values were observed at night (see Fig. 3). It was hypothesized earlier that the observed daily fluctuations of TTHM, CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub> are periodic.

Autocorrelation computes and plots the autocorrelations of a time series as a function of lags (every 4 h is considered a lag). In this study, the software Minitab is used to generate autocorrelation functions (acf) with  $\alpha = 0.05$ .

The coefficient of correlation remains high at nonzero lags, decreases slowly and increases again as the time shift approaches 24 h. This suggests some repetitions in fluctuation of content of over the 24-h period, a persistent trend in the fluctuation of THM concentrations. However, a random fluctuation unrelated to time is suggested if the correlation is maximal at lag zero, decreases to zero, and increases again between 4 and 6 h.

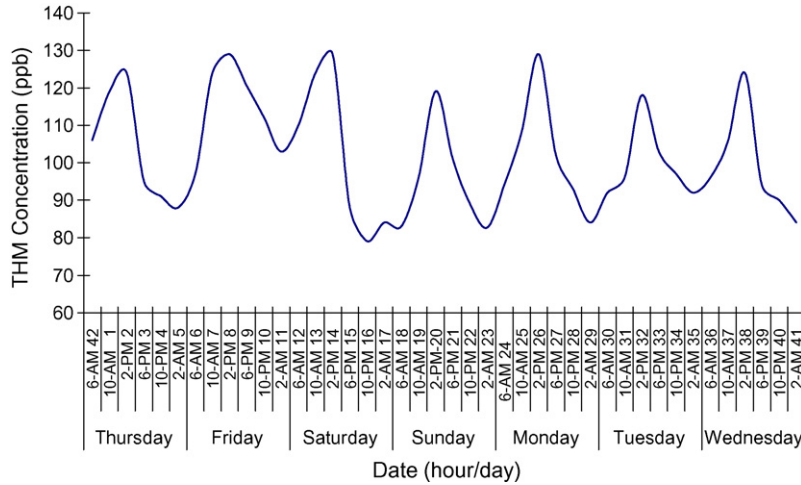


Fig. 1. Daily variation of TTHM in tap water at the clinic, Houston, Texas.

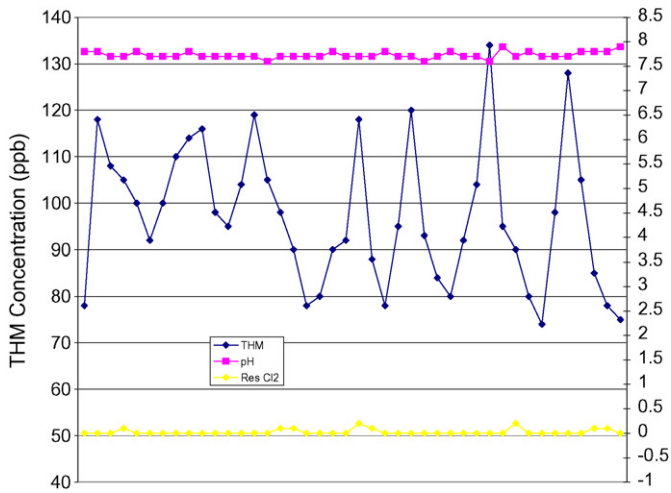


Fig. 2. Fluctuation of pH, residual chlorine and TTHM of tap water at the clinic, Houston, Texas.

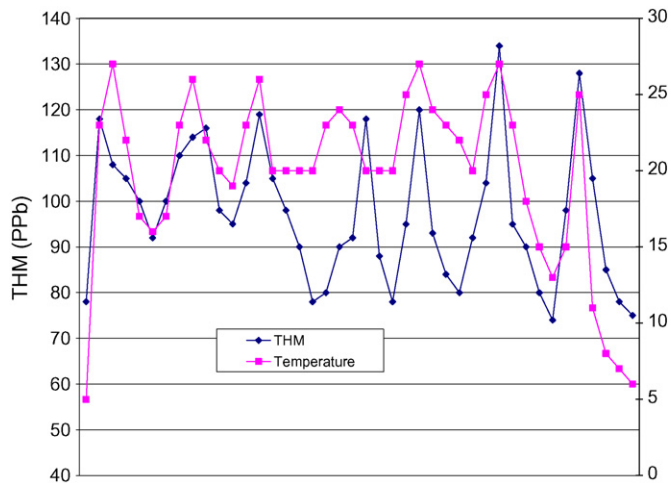


Fig. 3. Fluctuation of temperature and TTHM of tap water at the clinic, Houston, Texas.

In this study, autocorrelations are tested with *t*-statistics to show if they are different from zero, which means that the variables tend to be periodic. Absolute value of *t*-test greater than 1.25 for lags one through three, or greater than two for lags four and beyond, indicate autocorrelation values that are not equal to zero. The autocorrelation for all variables such as TTHM, CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub>, and temperature, and residual chlorine are developed. Figs. 4 and 5 present the autocorrelation curve derived for the TTHM and water temperature variables. They are always maximal at lag zero, a slow decrease was noticed and then an increase as the time shift approached 24 h. For the series of free residual chlorine, CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub> suggest a same pattern as TTHM and water temperature. For these time series as autocorrelation results show the coefficients of correlation high at zero, decreases and increases again as we approach the 24 h and then decreases again and the same pattern is repeated. This suggests some repetitions in fluctuation over the 24-h period; this persistence is statistically significant as revealed by the tests of autocorrelation with the *t*-statistic results of TTHM, chloroform, bromoform, dibromochloromethane,

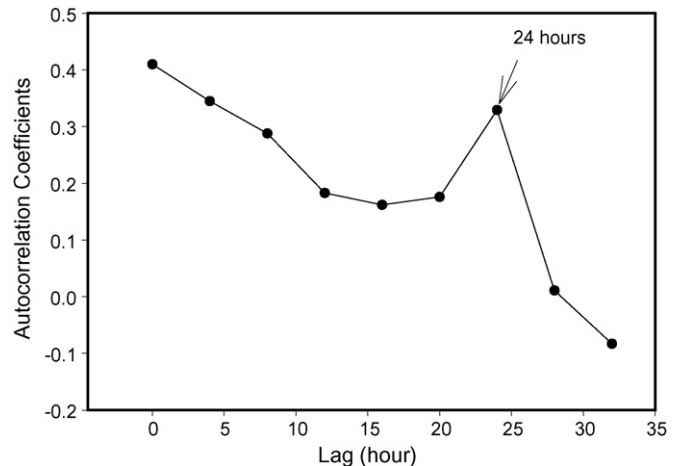


Fig. 4. Autocorrelation of TTHM level in drinking water at the clinic, Houston, Texas.

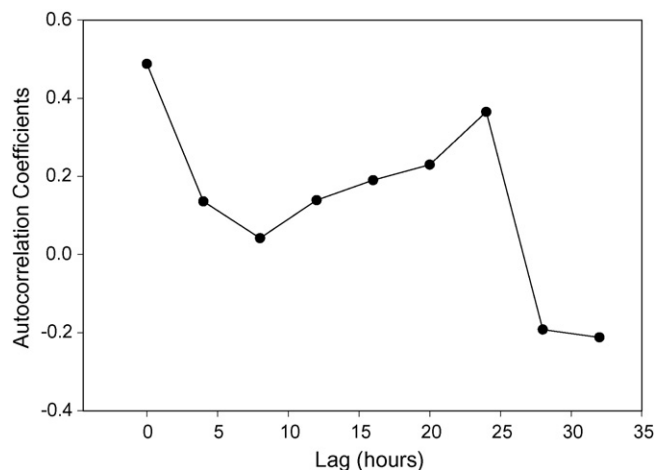


Fig. 5. Autocorrelation of water temperature level in drinking water at the clinic, Houston, Texas.

Table 3  
*t*-Statistic results of autocorrelation coefficients

Lag/ <i>t</i> -statistic	TTHM	pH	Temperature	Res.-Chlorine
0	2.24	0.12	3.16	3.24
4	1.68	0.64	0.76	2.35
8	1.0	-0.68	0.22	1.76
12	0.86	1.45	0.49	0.73
16	1.15	0.15	1.13	1.05
20	1.45	-0.21	1.17	1.4
24	2.05	0.42	1.36	1.7
28	-0.40	-0.49	0.89	1.3
32	-0.48	1.19	-0.96	0.32

dichloromethane, temperature and finally residual chlorine are summarized see Tables 3 and 4. However, for the time series of pH the correlation coefficient is maximal at zero lags, rapidly decreases to zero, and increases again between 4- and 6-h period. Such pattern suggests random fluctuation unrelated to time.

These results suggest that the variation in concentration is not an experimental variation but a real systematic phenomenon. It is probable that there is a systemic stagnation during the nocturnal hours, which would explain the higher concentration of THM detected in the morning hours. The lower concentration seen in the evening after heavy usage flushed the system would also be expected. We pronounce the system periodic and apply a

Table 4  
*t*-Statistic results of autocorrelation coefficients of trihalomethane compounds

Lag/ <i>t</i> -test	TTHM	CHCl <sub>3</sub>	CHBr <sub>3</sub>	CHClBr <sub>2</sub>	CHCl <sub>2</sub> Br
0	2.24	2.4	1.69	1.25	3.06
4	1.68	1.73	0.53	0.33	2.3
8	1	1.29	0.29	-1.33	1.39
12	0.86	1.49	-0.31	-1.07	1.15
16	1.15	1.07	-0.48	-0.37	1.26
20	1.45	1.18	-0.22	1.23	1.64
24	2.05	2.37	2.67	2.41	2.11
28	-0.4	0.32	0.22	-0.47	-1.09
32	-0.48	0.09	-0.29	0.19	-0.89

harmonic function model to describe the variation of THM concentration in the distribution system as a function of flushing and stagnation processes.

A harmonic equation was used as a regression model in conjunction with an iteration method to fit the data of the TTHM in tap water. Trihalomethane components follow the same concept

$$Y = Y_0 + a \sin \left[ \frac{2\pi t}{P} \right] \quad (3)$$

where  $Y$  is the TTHM level at any time of the day;  $Y_0$  the daily average value of THM during the 24-h period;  $a$  the maximum variation above and below the average, also called amplitude of the periodic function;  $P$  is the parameters defined by the curve fitting function of THM daily variation using iterative process (Sigma Plot) and they represent the cycle or period of the sinusoidal equation.

Up to 600 iterations are used to fit this type of equations. The iterative approach models every cycle (24-h period) separately. Therefore, 49 different sets of equations (7 cycles every week for 7 weeks) are formulated. These 49 different equations have different amplitude values ( $a$ ), different  $Y_0$ s and different parameters ( $P$ ). An example of this approach leads to the model illustrated in Eq. (4), which is significant and has an adjusted coefficient of determination of 0.799.

The final model is as follows:

$$\text{TTHM}_t = \text{TTHM}_a + a \sin \left( \frac{2\pi t}{24} \right) \quad (4)$$

where  $\text{TTHM}_a$  is the average value of TTHM concentration within each 24 h cycle.

The assumption is that the variance of independent variables is uniform. Constant variance tests were applied for all 49 equations developed and not one failed this test. This means that the harmonic equation model is a good fit for TTHM daily variation in the at the consumer tap water. The large adjusted  $R^2$ , the standard errors and the  $P$  value calculated for the regression model found in this study for all developed equations with no exception indicate that the developed model is a good description of the relation between the independent and dependent variables. These equations provide a statistically significant fit to the measured TTHM at any time during the 24-h period. For all the 49 equations, the minimum  $R^2$  value obtained was 0.94.

The period  $b$  of the developed model is included in the 95% CI of 24-hours (Fig. 6). This means that  $b$  and 24 are statistically the same, therefore the period of the model is shown again to be 24 and the new form of the model is as follows:

The amplitude variation " $a$ " of the periodic model was investigated as a function of daily temperature variation because the observed day-to-day variability of THM may be due to water temperature variation influencing the amount of chlorine added and the rate of THM formation. As it was shown earlier in Fig. 3, THM increases or decreases where an increase or decrease in temperature takes place, respectively. The same observation was made when we studied the entire period study (7 weeks) the daily peak of THM was higher when the daily temperature during that day was high.

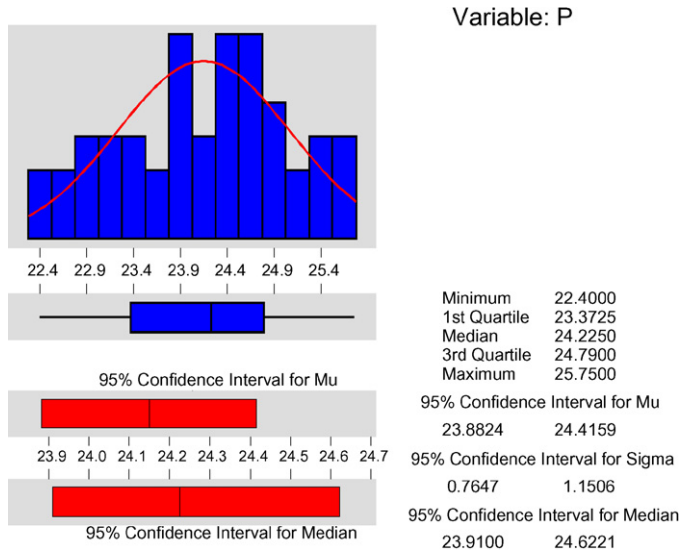


Fig. 6. Descriptive statistics of the parameter (*b*) of the developed model.

A regression equation is formulated below using the amplitude from the 49 developed models and water temperature from the database, and illustrated by Fig. 7.

Amplitude variation as a function of water temperature

$$a = Y_0 + bT \tag{5}$$

where *a* is the amplitude of THM daily variation model; *Y*<sub>0</sub> the linear regression intercept; *T* is the water temperature.

The resulting Eq. (6) for the amplitude is statistically significant (*P* = 142.0081) affirming that the amplitude is a linear function of water temperature with a correlation coefficient of 0.74

$$\text{The amplitude "a"} = 3.463 + 0.5365 \times \text{temp} \tag{6}$$

Combining with the above process, the final model defining the daily variation of THM is formulated as follows:

$$\text{THM}_t = \text{THM}_a + (3.463 + 0.5365 \times \text{temp}) \sin\left(\frac{2\pi t}{24}\right) \tag{7}$$

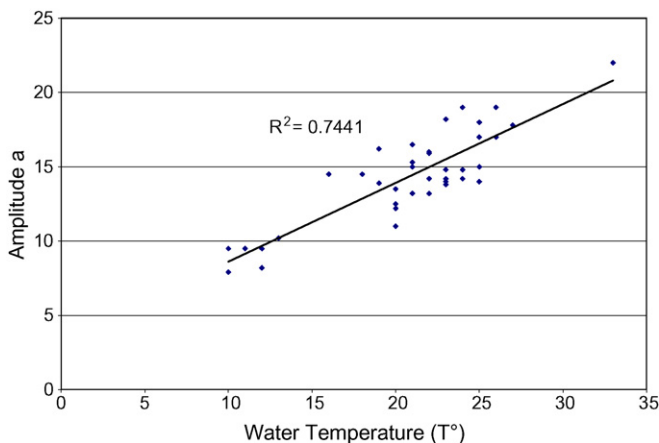


Fig. 7. Correlations between water temperature and amplitude of sinus model of THM variation.

where subscript *a* stands for average and subscript *t* stands for at any time of the day.

#### 4. Conclusion and discussion

In this study, we were able to examine the daily variation of temperature effects on levels of disinfection by-products along with the degree to which contaminant levels vary among households served by the same distribution system relative to the magnitude of variability over time within 24-h periods. To our knowledge, this is the first study that provides a quantitative estimation of daily effects of temperature on the variation in THM levels. Such a methodological model is beneficial in enhancing our understanding of the important sources of variation in levels of disinfection by-products in tap water and for assessing exposure when epidemiological studies are carried out.

While there has been some suggestion in the literature that variability in tap water THM levels may play a larger role than behavioral characteristics (for example, showering duration) in determining individual exposure, the relative influence of variation in water concentration and in patterns of water consumption and water use on individual exposure warrant further investigation. Our data and modeling results for THMs also indicate that variation from hour to hour is very influencing when it comes to choose a sampling strategy. As such, in the face of limited resources, a sampling strategy that collected greater numbers of quality assured measurements over time with fewer replicates collected at each sampling location would be more efficient and would likely yield improved estimates of (household) exposure.

The approach developed in this study incorporates more than one factor such as operating conditions and water temperature and proceeds with an iteration method to fit the harmonic model to explain the daily variation. The best fit was observed during the week days however, a slight deviation was observed during the weekend and this deviation may due to the operating conditions such flashing and stagnation time when the demand in weekend is a lot more than week days. The variation of the amplitude of the developed model was found to be a linear function of water temperature. The tests of autocorrelation with *t*-statistic results of TTHM, determine that CHBr<sub>2</sub>Cl, CHBrCl<sub>2</sub>, CHCl<sub>3</sub> and CHBr<sub>3</sub> follow the same trend as TTHM and will have the same model equation with different amplitude. We found greater association than reported previously because we have employed an iterative approach in addition to Box and Jenkins method that reduced estimation errors.

In conclusion, the new model predicts well the daily variation of TTHM concentrations because it employs all variables known to affect THM concentrations as a function of the operating mode and water temperature. The operating mode and temperature are related to water consumption trends to better describe the daily variation of TTHM in drinking water at the consumer's home. In our knowledge, the literature does not contain models that predict daily variation of TTHM at a specific location in the distribution system within 24-h time period. We assert that the model formulated here will lead to more realistic risk estimates from drinking water at specific sites throughout the distribution system.

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