Monitoring and modeling of trihalomethanes (THMs) for a water treatment plant in Istanbul

V. Uyak*, I. Toroz, S. Meriçb

*Department of Environmental Engineering, Faculty of Civil Engineering, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey
Tel. +90 (212) 285-6548; Fax: +90 (212) 285-3781; email: uyakov@itu.edu.tr / vuyak@hotmail.com
bDepartment of Civil Engineering, University of Salerno, 84084 Fisciano (SA), Italy

Received 19 October 2004; accepted 29 October 2004

Abstract

Because of increasing concern for both microbial control and disinfection by-products (DBPs) formation, water utilities are strictly examining and optimizing disinfection practices. In this study, modeling of trihalomethanes (THMs) formation at processed water of the Kagithane water treatment plant in Istanbul City was conducted. Data for THMs and other water quality and operational parameters were generated through a 12-month sampling program between January and December 2003. A multiple linear regression model was developed to predict THMs concentrations in processed water. Routinely measured parameters including total organic carbon (TOC), pH, temperature, and chlorine dose were used to develop the model for the prediction of THMs. Both pH (r = 0.963) and temperature (r = 0.921) were found to be the parameters of the highest statistical significance as predictors for THMs occurrence. The regression analysis resulted in a model that is directly applicable to the chlorination of raw waters. This indicated that the linear models developed could be used to estimate THMs concentration for different water quality and treatment processes with different operational conditions.

Keywords: Disinfection by-products (DBPs); DBP models; Trihalomethanes (THMs); Processed water; Water treatment, Istanbul

1. Introduction

Disinfection is the most important process in the treatment of drinking water supplies since it removes or inactivates pathogenic microorganisms responsible for waterborne diseases such as cholera and dysentery [1]. Chlorination is a widely used disinfection method because of its very efficient and cost-effective properties [2].

*Corresponding author.
Almost all municipal water supply systems in Turkey also use chlorine for water disinfection. However, it was discovered that the use of chlorine as an oxidant or disinfectant posed potential health risks due to the formation of carcinogenic halogenated organic compounds known as disinfection by-products (DBPs) [3,4]. Among DBPs found in chlorinated water, trihalomethanes (THMs) have been the focus of particular attention because they are considered potentially carcinogenic for the bladder [5]. The United States Environmental Protection Agency (USEPA) [6] has defined the hazardous classes for different DBPs among THMs, HAAs and inorganic DBPs; CHCl₃, CHBr₂Cl and CHBr₃ were classified as possible carcinogens to humans. Also, recent studies have suggested links between adverse reproductive outcomes and exposure to THMs during pregnancy [7,8].

Concerns about health risks associated with THMs have prompted several industrialized countries to establish maximum acceptable levels for THMs concentrations in drinking water [9]. The US EPA developed the Disinfectants/DBP (D/DBP) Rule in 1998 to set a maximum contaminant level (MCL) of 80 µg/L for THMs in drinking water [10]. Moreover, recently most of the European countries regulated THMs in their water at the MCL of 100 µg/L [11]. However, up to now, there is no MCL for DBPs, especially for THMs in Turkish Drinking Water Regulations (TS-266) [12].

THMs formation during water treatment processes is important and needs to be monitored. The modeling of THMs consists of establishing empirical or mechanistic relationships between THM levels in treated water and the water quality and water treatment operational control parameters (such as chlorine dose applied, temperature, pH).

The model equations developed for chlorination were based on raw water chlorination and not chlorination of treated waters (e.g., coagulated-settled waters or granular activated carbon (GAC)-treated waters), which are most appropriate for prechlorination [13]. Efforts are currently underway to develop predictive equations based on reaction kinetics of DBP formation that will be appropriate to coagulated-settled waters and may remove some of the restrictions regarding boundary conditions [14]. The progress in development of new models by Abdullah et al. [15], Elshorbagy et al. [16], Golfinopoulos et al., [17], Golfinopoulos and Arhonditsis [18], Gallard and Gunten [19], Milot et al. [20], and Sohn et al. [21] have contributed to explaining the effect of water characteristics on THM formation as well as to optimize the coagulation process which is essential for water treatment.

This paper presents the development of a linear multi-parametric THM predictive model with a particular focus on the Kagithane Celebi Mehmet Han water treatment plant (KWTP) in Istanbul, Turkey, which supplies the water needs of more 1 million people on the European side. The model was based upon raw water characteristics; e.g., TOC, pH, temperature and sum of applied pre- and final chlorine doses, to predict the THMs in processed water. The developed model was then validated using THM data sets obtained from the same treatment and from the Buyukcekmece water treatment plant that has different raw water characteristics and treatment plant configuration than in Istanbul. The major importance of the developed model is that it was the first investigation in this field in Turkey where most of the water treatment plants apply prechlorination.

2. Materials and methods

2.1. Description of water treatment plant

In this study, KWTP, which supplies the water needs of more than 1 million inhabitants, and is operated by the Istanbul Water and Sewerage Administration, was selected to monitor and model THMs formation. The KWTP receives surface water mainly from the Alibeykoy
Reservoir and Terkos Lake, and daily services 300,000 m$^3$ of water to the city. The treatment plant consists of prechlorination (1.5 mg/L), coagulation by the addition of 40 mg/L alum, flocculation, sedimentation, high-speed sand filtration with a backwashing period of 30–36 h, and final chlorination (typically up to 3 mg/L). The raw water of this plant was found to be relatively unpolluted with a 4.86 mg/L of TOC mean concentration and low turbidity (<7 NTU). Quality parameters of raw water and processed water used for model development are shown in Table 1.

2.2. Sampling procedure and field measurements

A 12-month sampling program was carried out from January to December 2003. Water samples were taken from influent and processed water of the treatment plant. On the other hand, in order to monitor and draw a picture of THMs in distribution systems, several samples were taken from distribution networks. For distribution systems, 72 water samples were taken and sampling was done in official buildings and grocery stores using faucets in the washrooms.

For THMs measurements, tap water was collected in 300-mL amber glass bottles and the residual chlorine was blocked by adding sodium thiosulphate penta-hydrate. During the sampling, the bottles were filled without passing air bubbles through the sample. The THMs bottles were previously washed with detergent and rinsed with deionized water and ultra-pure water, and placed in an oven at 400°C for 1 h. Once collected, samples were carefully stored in the dark at 4°C and carried to the laboratory for analytical procedures.

Samples for TOC measurements were collected in 250-mL plastic bottles. Measurements of pH and temperature were carried out simultaneously in the field using a solid selective electrode connected to a WTW multimeter model pH meter.

2.3. Determination of THMs

Chlorinated volatile organics in the aqueous phase can easily be extracted using pentane as an extraction solvent [22]. In this study, THM measurements were performed using the EPA 551 method [22]: 35-mL THMs samples were pipetted into 40-mL screw cap vials. Then 8 g of reagent grade sodium sulfate (Na$_2$SO$_4$) was added to the extraction vial to increase the ionic strength of the aqueous phase, thus increasing the partitioning of THMs to the pentane phase and decreasing the water solubility of pentane. Then, 3 mL of pentane were transferred to each vial. The vials were then shaken vigorously for 1 min and allowed to stand for 3 min to facilitate phase separation. The pentane extract was removed
Table 2
Characteristics of GC–ECD analysis

<table>
<thead>
<tr>
<th>Analytical column:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>DB 1</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>J&amp;W Scientific Folsom CA</td>
</tr>
<tr>
<td>Type</td>
<td>Fused silica capillary</td>
</tr>
<tr>
<td>Length, m</td>
<td>30</td>
</tr>
<tr>
<td>Internal diameter, mm</td>
<td>0.32</td>
</tr>
<tr>
<td>Film thickness, μm</td>
<td>1</td>
</tr>
<tr>
<td>Injector:</td>
<td></td>
</tr>
<tr>
<td>Injection volume, μL</td>
<td>2</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>200</td>
</tr>
<tr>
<td>Detector:</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>μECD</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>300</td>
</tr>
<tr>
<td>Oven temperature program:</td>
<td>35°C, hold 9 min; increase @ 1°C/min for 5 min, 40°C hold 3 min; increase @ 6°C/min for 13 min; 120°C, hold 2 min; increase @ 60°C/min for 0.5 min; 150°C, hold for 5 min</td>
</tr>
<tr>
<td>Carrier gas:</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Make-up flow, mL/min</td>
<td>58.7</td>
</tr>
<tr>
<td>Carrier flow, mL/min</td>
<td>1.3</td>
</tr>
</tbody>
</table>

using a Pasteur pipette and transferred to a 1.8-mL vial. Then, 2 μL of extract was analyzed by gas chromatography (GC) (Hewlett Packard Gas, 6890 Series II) with an electron capture detector (ECD) and capillary column. The system was supported by a HP Chemstation software. The carrier gas used was helium and the make-up gas was nitrogen. The column used for the GC electron capture detector (GC–ECD) analysis was fused silica DB-5, 30 m × 0.32 mm ID × 0.30 μm film thicknesses. The injection technique was split/splitless, and the carrier gas flow was 1.6 mL/min. Detailed information regarding the GC–ECD analysis is shown in Table 2. The minimum reporting levels obtained with this method are 0.1 µg/L.

2.4. Determination of TOC

TOC measurements were performed with a Shimadzu TOC-5000 analyzer equipped with an auto-sampler, according to the combustion-infrared method as described in the Standard Methods [23]. The sample was injected into a heated reaction chamber packed with a platinum-oxide catalyst oxidizer to oxidize organic carbon to CO₂ gas. Inorganic CO₂ was measured by a non-dispersive infrared analyzer and related to an equivalent concentration of organic carbon.

2.5. Data analysis and model development

Due to the rapid chemical changes that occur in water samples during transit and storage, certain parameters (temperature and pH) were measured on site, immediately after the sample was taken. The chlorine dose applied as the sum of pre-chlorination and final chlorination doses was obtained from treatment plant. To investigate the occurrence of THMs in processed water within the water distribution system, an intensive 12-month sampling program was undertaken between January and December 2003.

The model development was based on raw water TOC, pH, and temperature values, and the sum of prechlorination and final chlorination doses for correlation with the finished water THMs values. The Kolmogorov–Smirnov test was used to test the variables for normality, and the Pearson correlation coefficient was used to measure the strength of the relationship between variables. Before model construction, log transformations were applied to all data. Then, a multiple linear regression model for THM formation was created using a statistical package for social sciences (SPSS) software [24]. Multiple regression analysis was applied to evaluate the statistically significant variables of the system. The level of significance (α) for the inclusion of a variable in the model was 0.05. Throughout the process of model development, several linear and
non-linear regression analyses were performed. Independent sets of data from different sources were collected to validate the model. The model’s validation confirmed that it is sound and effective. In addition, the model validation requires assessing the effectiveness of the fitted equation against an independent set of data, and it is essential if confidence in the model is to be expected. In this study a total 120 samples was collected from raw and processed water for the purpose of model development and validation.

3. Results and discussion

3.1. THM formation modeling

During the model studies period, a total of 120 samples was collected from the KWTP and its distribution networks for the year 2003. The statistical summary of raw and processed water quality parameters are shown in Table 1. The TOC concentration in raw water ranged from 4.20 to 6.20 mg/L, while the pH varied from 7.10 to 7.90. The applied chlorine dose levels in the water treatment plant varied between 2.82 to 6.75 mg/L, and the raw water temperature ranged from 7.20 to 22.70°C. TOC, pH, and the temperature of water samples were in detectable range, and they could be quantified in all these samples. Chloroform constituted the major component in THMs (>90% of total THMs) followed by dibromochloromethane. The mean value of THMs and chloroform in processed water ranges from 48.00 to 102.00 μg/L and 42.20 to 95.90 μg/L, respectively. The standard deviation for THMs and chloroform in processed water is 18.02 and 17.00 μg/L, respectively.

On the other hand, statistical information of THMs and chloroform at three different sampling points of distribution systems are shown in Tables 3 and 4, respectively. Table 3 shows that the mean value of THMs ranges from 86.0 to 92.4 μg/L, while the standard deviations for THMs at these sites vary between 25.4 and 29.6.

### Table 3
<table>
<thead>
<tr>
<th></th>
<th>Sp-1</th>
<th>Sp-2</th>
<th>Sp-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>56.3</td>
<td>58</td>
<td>59.6</td>
</tr>
<tr>
<td>Maximum</td>
<td>132.6</td>
<td>134.9</td>
<td>147.8</td>
</tr>
<tr>
<td>Mean</td>
<td>86</td>
<td>88.3</td>
<td>92.4</td>
</tr>
<tr>
<td>SD</td>
<td>25.4</td>
<td>26</td>
<td>29.6</td>
</tr>
</tbody>
</table>

In addition to this, Table 3 shows that the mean value of chloroform ranges from 79.5 to 83.8 μg/L, and its standard deviations at those sites varies between 24.6 and 27.3 μg/L.

3.2. Effect of TOC

Using the Pearson correlation test, a strong relationship ($r = 0.900$) was obtained between THM formation and TOC for KWTP, as shown in Table 4. Most researchers showed that THM formation rose with increasing soluble humic material in surface water. Besides, the rate of THM formation is equal to that of TOC consumption, and a first-order reaction was reported with respect to TOC [20, 21]. Moreover, a higher level of available TOC will provide more THMs if enough residual chlorine is available.

It was noted that fulvic acids account for over 90% of the aquatic humic in many water sources. According to Babcock and Singer [27], the relative contributions to THM production came from humic fraction than fulvic fraction since the
former reacts more readily with chlorine. As a consequence of slow reaction between THM precursors and chlorine, THM formation is a second-order reaction with respect to TOC, especially for long-term THM formation [31]. Thus, THMs formation can be explained as a multi-stage reaction pathway involving an initial fast reaction of chlorine with the TOC to produce chlorinated intermediates, which may then undergo further slow reaction by several possible pathways to produce THMs and other by-products [30].

3.3. Effect of pH

The Pearson correlation test was applied to examine the correlation of THMs with respect to pH measured at raw water. A high level of correlation \( r = 0.963 \) was obtained between THM concentration and pH for KWTP processed water. Generally, the rate of THM production increases with pH [25]. Kavanough reported a three-fold increase in the reaction rate per unit pH [20]. Adin and coworkers found that pH has two effects: decreased pH resulted in low THMs formation and similarly increased pH results in high THM formation [26]. The lower the pH, the higher the HOCI concentration, resulting in a shift to a higher concentration of humic substances. Several investigators stated this effect, and they reported decreased THM formation as a result of lowering the pH [28]. Garcia-Villanova et al. [29] reported that there was a linear relationship between pH and THM formation, as was the case with our modeling studies. Moreover, this parameter seems to be very important in controlling THM formation.

3.4. Effect of chlorine dose applied

Attempts were made to determine the effect of applied chlorine dose (prechlorination and final chlorination) on the production of THMs in processed water. Using the Pearson correlation method, a strong definite relationship \( r = 0.879 \) was obtained between THMs production and applied chlorine dose for our study (Table 5). As reported previously, chlorine addition to water leads to the formation of HOCI and a hypochlorite ion \( (OC1^-) \) [1]. The formation of these two species depends on the pH. In acidic solution the formation of HOCI dominates, whereas in the alkaline solution \( OC1^- \) is dominant. In our study the pH value of the raw water ranged from 7.00 to 7.90, and in this range HOCI is the more prevalent chlorine species which is responsible for the formation of THMs; when THMs concentration increases, the concentration of HOCI decreases, which in this case is also the residual chlorine [1].

3.5. Effect of temperature

Pearson regression tests indicated a strong correlation between temperature and the formation of THMs. A strong correlation \( r = 0.921 \) was obtained between THM production and temperature for the study area. Temperature can have a significant effect on THM formation. Seasonal variations in temperature can affect reaction rates. In our study the temperature value of the drinking water ranged from 7.20°C to 22.70°C, which was associated with the formation of THM values in a wide range of 48.0 µg/L to 102.0 µg/L. A study by Knocc et al. [30] indicated that the rate of THM formation at 2°C was normally 60–70% less than observed at 22°C.

3.6. Proposed THM model

Using a SPSS statistical program, a THM model was developed and THM concentration in processed water was predicted from raw water TOC, pH, temperature values and applied sum chlorine dose. After log-transformation of all variables, the linear regression model obtained for this study is as follows:

\[
DWR-748
\]
Table 5
Pearson correlation matrix for water quality and operational parameters

<table>
<thead>
<tr>
<th></th>
<th>TOC</th>
<th>pH</th>
<th>Applied Cl₂</th>
<th>Temperature</th>
<th>THMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0.884</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied Cl₂</td>
<td>0.935</td>
<td>0.909</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>0.847</td>
<td>0.924</td>
<td>0.913</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>THMs</td>
<td>0.900</td>
<td>0.963</td>
<td>0.879</td>
<td>0.921</td>
<td>1.000</td>
</tr>
</tbody>
</table>

\[ \log \text{THMs} = -1.115 + 1.314 \log (\text{TOC} + 3.2) \]
\[ + 1.496 \log (\text{pH} 4.0) - 0.197 \log (\text{dose} - 2.5) \]
\[ + 0.724 \log (\text{temp.} + 10) \] (1)

Then, the log-model in its transformed variable was modified by taking antilogs of both sides, and the resultant regression model obtained for the study area is:

\[ \text{THMs} = 7.07 \times 10^{-2} (\text{TOC} + 3.2)^{1.314} \]
\[ (\text{pH} 4.0)^{1.496} (\text{dose} - 2.5)^{-0.197} (\text{temp.} + 10)^{0.724} \] (2)

where TOC is expressed in mg/L, the dose is the chlorine (pre-chlorination plus final chlorination) expressed in mg/L, and temperature (temp.) is expressed in °C. The model accuracy is shown in Table 6, and it was found to be statistically significant for all four variables. Moreover, all the adjusted coefficients of determination \( R^2 > 0.5 \) were satisfactory. We can also assume from the normal probability plot of Fig. 1 that the cumulative probability measured and observed values approach normal distribution, as all the points are near the straight line, which is the identical situation of normality [26]. The model coefficients and their level of significance are also shown in Table 7.

On the other hand, Fig. 2 shows the normal probability plot of measured vs. the predicted values for THMs in 2003. In this figure, all the points are near the straight line with a \( R^2 \) value of 0.96. In addition, Fig. 3 demonstrates the comparison of measured and predicted THMs values. As seen in this figure, the predicted THM curve overlaps the measured THM curve in most cases. Moreover, model predictions appear to be most accurate for our study.

![Fig. 1. Normal probability plot of measured vs. the predicted cumulative probability values for THM in 2003.](DWR-748)
Table 7
Regression coefficients, standard errors, and t-values for the variables included in the proposed THM model

<table>
<thead>
<tr>
<th>Variables</th>
<th>β</th>
<th>Standard errors</th>
<th>t-values</th>
<th>p-level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>-1.115</td>
<td>0.318</td>
<td>-3.511</td>
<td>0.010</td>
</tr>
<tr>
<td>log (applied Cl2-2.5)</td>
<td>-0.197</td>
<td>0.043</td>
<td>-4.587</td>
<td>0.003</td>
</tr>
<tr>
<td>log (pH-4.0)</td>
<td>1.496</td>
<td>0.398</td>
<td>3.757</td>
<td>0.007</td>
</tr>
<tr>
<td>log (T+10)</td>
<td>0.724</td>
<td>0.155</td>
<td>4.678</td>
<td>0.002</td>
</tr>
<tr>
<td>log(TOC+3.2)</td>
<td>1.314</td>
<td>0.381</td>
<td>3.445</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Table 8
Quality parameters of raw and processed water from the Buyukcekmece water treatment plant [33]

<table>
<thead>
<tr>
<th>Variables</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC, mg/L</td>
<td>3.86</td>
<td>6.75</td>
<td>5.36</td>
<td>2.04</td>
</tr>
<tr>
<td>UV_{254}, 1/cm</td>
<td>0.154</td>
<td>0.232</td>
<td>0.193</td>
<td>0.06</td>
</tr>
<tr>
<td>Alkalinity, mg CaCO3/L</td>
<td>108</td>
<td>156</td>
<td>132</td>
<td>33.94</td>
</tr>
<tr>
<td>pH</td>
<td>7.45</td>
<td>8.40</td>
<td>7.93</td>
<td>0.67</td>
</tr>
<tr>
<td>Applied Cl2, mg/L</td>
<td>2.95</td>
<td>7.20</td>
<td>5.08</td>
<td>3.00</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>7.30</td>
<td>23.10</td>
<td>15.20</td>
<td>11.17</td>
</tr>
<tr>
<td>THMs in processed water, μg/L</td>
<td>78.0</td>
<td>138.0</td>
<td>108.0</td>
<td>42.4</td>
</tr>
</tbody>
</table>

Fig. 2. Measured THM values vs. predicted THM values in 2003.

3.7. Model validation

The Buyukcekmece water treatment plant (BWTP), which also applies pre- and post-chlorination with different water characteristics (Table 8), was the case for the validation of the model developed in this study. The reason for choosing BWTP for validation was due to its high bromide content (>150 μg/L) and high pH, which would be useful for the application of a model developed for a different water origin. In addition, this was consistent with previous findings that the yield of THMs was reported to increase with increasing pH [32]. Qualitatively, a visual inspection of a plot of measured values vs. predicted values can serve as a measure of model fitness [26]. The fit was evaluated through examination of various statistical indicators, including $R^2$ and the F-statistic, while validation focused on the slope and the intercept of predicted vs. measured values, $R^2$ [26]. The results of the validation analysis are given in Fig. 4, which shows the measured vs. predicted THMs values in processed
water. The model validation indicates reasonable predictions of THMs with $R^2$ value of 0.86.

4. Conclusions

THMs are formed during the chlorination of waters containing humic substances. Changes in temperature, pH, TOC concentration, and applied chlorine dose directly influence THM concentrations in processed water. This article discusses the formulation of a model for predicting THM levels in processed water of a water treatment plant in Istanbul subjected to chlorination. With the use of multiple linear regression techniques, it is possible to develop models for simulating and predicting THMs during water treatment. This research resulted in a model that is directly applicable to the chlorination of raw waters. The model described above can be used to estimate
THM concentration for different water qualities and operational conditions in processed water where chlorination is the only treatment in the process. Based on the validation results obtained, it can be stated that the model is the most applicable to chlorinated waters. This indicates that the linear model developed could be used to estimate THM concentration for different water quality and operational conditions where chlorination is the only treatment in the process. Due to the fact that very little data about THMs are currently available for the distribution system in Istanbul, the generation of data using a modeling approach is very useful. However, with given complexity of water quality and evolution in distribution systems, modeling results must be interpreted with caution.

Acknowledgements

The authors would like to thank the Water Quality Laboratory of the Istanbul Water and Sewerage Works Administration for its collaboration of sampling and transportation. The contribution of the referees (Ceyda Uyguner and Natasa Nikolaou) is appreciated.

References