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# Determination of trihalomethanes levels in a selected area of Amman's drinking water distribution system: case study

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#### ABSTRACT

Water quality model is a helpful management tool for water distribution system. Estimation of growth coefficients is an important and challenging component of water quality modeling. Reactions occurring in the bulk flow for both trihalomethanes (THMs) formation and chlorine decay kinetics in Zai drinking water have been studied. It was found that both THMs and chlorine kinetics follow first-order reactions for growth and decay, respectively. A numerical model for predicting THMs formation in drinking water distribution system networks has been developed and applied. THMs measurements were taken at three locations over 106 h from a northern portion of Sport City area (Kharabshe Reservoir), while the water quality time step is set to 3 min, to insure predicting accurate total trihalomethanes (TTHMs) concentrations. The bulk flow for TTHMs formation rate constant value is determined and set to  $5.82 \times 10^{-2}$ /h. The modeled results for THMs formation in the field network were compared favorably with the observed data for three sampling points in the network. The THMs formed inside the selected network of this case study was sixfolds higher than that formed in Zai treatment plant; and 113% higher than that formed in Kharabshe Reservoir. The model proved to be an effective tool for prediction of THMs formation in drinking water distribution systems.

*Keywords:* THMs formation kinetics; Chlorination; Chlorine decay kinetics; Drinking water distribution system; Water quality model

# 1. Introduction

Most of West Amman drinking water is obtained from the King Abdullah Canal after treatment. Since most of this Canal's water is collected from surface run-off and transported in an open atmosphere over 60 km in the Canal. During this journey, the water is contaminated and polluted by man and nature. Therefore, water treatment plant must be available. The Zai water treatment plant was put into service in 1985. This plant receives raw water from King Abdullah Canal, and pumps treated water to a terminal reservoir which serves the West Amman area and feeds other downstream tanks. Various chemicals are added to water to regulate the level of chemical contaminants and pathogenic micro-organisms. Each of these chemicals has by-products and residuals that may lead to substantial changes in water quality while being transmitted through the distribution system

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before reaching the consumers tap. It has been reported that the high concentrations of added chlorine as well as other parameters may have resulted in greater THMs formation [1,2].

Analytical kinetic models of THMs formation have not been developed mainly because of the complexity of the reactions of chlorine with organic materials in water. The consumption of chlorine in water occurs through complex sequential and parallel reaction pathways with unknown rates [3]. The consumption of chlorine by reaction with organic and inorganic chemicals in the bulk aqueous phase is reasonably well defined and characterized as a simple first-order decay reaction [4].

During the last few decades, considerable attention has been focused on the development of algorithms for use in modeling water quality in water distribution systems. The algorithms developed have used both steady-state formulations and dynamic model formulations. These models incorporate hydraulic simulation of flows and pressures in the system with equations to predict concentrations of water quality constituents. A steady-state model based on mass conservation principles was proposed in 1985 to determine the spatial distribution of dissolved substances at constant hydraulic conditions [4].

A model that tracks the propagation and decay or growth of a constituent as it travels through a piping network under steady or time varying flow conditions has been proposed in 1987 [5]. A dynamic approach for modeling of a distribution system's water quality was developed in 1988. The distribution system is represented by a link-node system in which the link represents a pipe section linked to the system at junctions called nodes [6–8].

Moreover, in 1994, a mass-transfer model was developed to describe the chlorine decay in pipe networks that applies to unsteady flow under both turbulent and laminar flow conditions. The model considers first-order reaction of chlorine to occur both in the bulk flow and the pipe wall. The model has been translated into a computer program called EPANET [9].

In 1997, a new computer model using an inverse method was presented to directly calculate the source chlorine concentrations required to meet specified chlorine residuals at a particular point in the pipe network, unlike the direct simulation [10].

The main objective of this work is to gain a better understanding of the kinetic relationships describing chlorine decay and THMs formation in drinking water distribution system. In addition, an algorithm is adapted to simulate the change in THMs concentration at various water end-points in a selected part of the drinking water distribution system in West Amman Area.

# 2. Materials and methods

# 2.1. THMs formation test data

The kinetics of THMs formation in the bulk phase were determined by conducting long-term bottle tests (i.e. batch testing of samples held in dark bottles over increasing time periods).

The procedure is based on collecting a 2 liters sample from the effluent stream of Zai water plant. This sample is stored at a given constant temperature. After each time intervals, a sample for THMs measurement was taken from the original sample in a 40 ml septum vial filled to zero head space and containing a few crystals of soduim thiosulfate (to eliminate any residual chlorine and thus stop the trihalomethane formation reaction) and stored in the dark at temperatures between 0 to 4°C prior to analysis. The THMs were measured using the Head Space Analyzer GC HS 2000 (Thermo Quest) with ECD, where, sample is placed in a septum vial and allowed to equilibrate with its head space vapor at 50°C. The vapor of sample is injected automatically by head space analyzer into a packed column gas chromatograph fitted with an electron capture detector. Heluim was used as the carrier gas, the splitless injector was maintained at 185°C with split flow 40 ml/min, and the oven programed from 60 to 150°C at a rate of 10°C per minute. The ECD temperature is 350°C with make-up gas flow of 30 ml/min. The concentrations of THMs were determined at specified conditions (temperature 16 °C, pH 7.8, TOC 1.14 ppm, free chlorine 1.04 ppm, and bromide ion 0.42 ppb)and at different times.

## 2.2. Chlorine decay test data

DPD-colorimetric method was employed for the measurement of residual chlorine measurement. The procedure is based on collecting 2 liters samples from the effluent of Zai water plant. The samples are stored in the dark at certain constant temperature. For each measurement, a small sample (5 ml) is taken from the original sample. The residual chlorine is determined at specified conditions. In this study, the measurements were made at a temperature 16 °C, pH = 7.8, TOC 1.14 ppm, and bromide ion 0.42 ppb at increasing periods of time.

## 2.3. Field study network configuration

The northern portion of the Sport City region in Amman (Kharabshe Reservoir area) was selected for this study since it is relatively small isolated zone with a single source of water. A schematic diagram of this network is shown in Fig. 1.

The general chart of the water quality simulation algorithm steps is shown in Fig. 2. However, the key inputs to a water quality model are physical characteristics of pipe network such as diameter, length, and location of pipes, water demands throughout the system, initial water quality concentrations, and decay or growth coefficients for water quality reactions. The full specifications of this selected water distribution network are shown in Table 1.

In the choice of sampling points in the network, attention was paid to the criterion of establishing points close to the reservoir and others from it. Three sampling points were selected using the following criteria: the water flowing in the selected network must be exclusively from the reservoir; the selected points should be uniformly distributed along the network to represent short and long residence time from the outlet of the reservoir; and they should all be supplied by the same main pipe.

#### 2.3.1. Sampling study description

The analysis of the water samples taken from the study field and the sampling locations were performed in Water Authority Central Laboratories. Standard protocols were followed to ensure that the samples were preserved prior to analysis. For some constituents, this required fixing, immediate refrigeration, and shipment to the laboratory.

The primary data required for the analysis and modeling phase were time series sampling information on THMs concentrations at selected sampling locations within the study area. Accordingly, 19 samples were collected at different times at three sampling points and analyzed for THMs. The sampling was performed over a 106 h period towards the end of March, 2010. The pumps supplying this network were turned on at 12:00 noon on March 24 and turned off at 12 noon on March 28, 2010. Samples were taken at approximately 8h intervals at three sampling locations and were analyzed for THMs. In most cases, temperature readings were taken using a digital thermometer.

#### 2.4. Hydraulic calibration

Throughout the sampling study period, no tracer was added to the water source as part of general policy of the Water Authority not permitting the addition of foreign tracers. The network representation of the study field was specified and known previously by the Water Authority supplying the northern portion of the Sport City region in Amman (Kharabshe Reservoir area). The field network's data acquisition system provides the water levels in the tank and the source flow. Consequently, this data are used to determine the expected hourly demand pattern during the sampling period for the field consumers supplied by the selected network. The tank water level values obtained from the data recording system are employed to investigate the hydraulic



Fig. 1. A schematic diagram of the field network.



Fig. 2. General chart of water quality algorithm steps.

calibration by comparing the time predicted water levels to the observed values. The results of this comparison between observed and predicted water levels in Kharabshe tank are shown in Fig. 3.

# 3. Water quality model development

A mathematical-based dynamic water quality model has been developed and applied in the present work. This model is based on the principle of conservation of mass coupled with reaction kinetics to determine the movement and transformation of chlorine constituents in the water column (bulk flow reaction) under time varying conditions [5,9,11].

The focus of the present research model is on THMs formation based on the kinetics data of the treated water samples taken from the effluent water from Zai water treatment plant. These kinetics used in the developed model can effectively track the transport and propagation of THMs levels in water distribution networks. Three processes are involved as a constituent moves through a network:

Pipe no.	From node	To node	Pipe flowrate (m <sup>3</sup> /h)	Pipe length (m)	Pipe diameter (m)
1	1	2	24.00	150	0.1016
2	2	3	23.47	150	0.1016
3	3	4	1.07	50	0.0762
4	4	5	0.27	20	0.0762
5	3	6	21.93	180	0.1016
6	6	7	0.90	60	0.1016
7	7	8	0.63	40	0.1016
8	8	9	0.47	50	0.0508
9	9	10	0.27	90	0.0508
10	6	11	18.63	175	0.1016
11	11	12	1.47	50	0.1016
12	12	13	1.27	50	0.1016
13	13	14	1.09	50	0.1016
14	14	15	0.91	50	0.1016
15	15	16	0.73	50	0.1016
16	16	17	0.54	50	0.1016
17	17	18	0.36	130	0.0508

Table 1 The specifications of the field network



Fig. 3. Kharabshe reservoir modeled and observed water tank levels.

- Convective flow in a pipeline.
- Chemical reaction (decay or growth over time).
- Mixing at pipeline junction nodes.

Longitudinal diffusion of the constituents into the carrying water is considered to be small relative to the bulk convection and it is, therefore, neglected.

The distribution system is represented by a pipe link node system. Demands and inflows (both volumes and concentrations) are assumed constant over a user-defined period. Thus, the flow and velocity for each link is known for each period. Each period is divided into an integer number of time steps. Once the time step is determined, the number of segments in a pipe link is computed as the largest integer less than or equal to the pipe's travel time divided by the time step. The length of a segment may vary from a pipe link to another or for a pipe link at different time period.

The transport and propagation of a constituent in a pipe section can be represented by the general mass conservation equation

$$\frac{\partial C}{\partial t} + (V \cdot \nabla C) - (D\nabla^2 C) = R(C)$$
(1)

Plug flow conditions most closely approximate the actual system in a pipe section and will be assumed in the material balance. The flow is assumed turbulent and the velocity profile is nearly uniform across any pipe section. Turbulent flow conditions will promote radial mixing and therefore nearly uniform constituent concentrations are assumed at any cross-section.

The flow is assumed to be one-dimensional in the axial *z*-direction in the pipe link; and since longitudinal diffusion of a constituent in the flowing water is small relative to the bulk convection, it is thus neglected. The one-dimensional convection diffusion equation of a constituent in water flowing through a section of a pipe becomes:

$$\frac{\partial C}{\partial t} + v_z \frac{\partial C}{\partial z} = R(C) \tag{2}$$

To solve Eq. (2), it is important to obtain the steady-state solution as this will be used as an initial condition for the unsteady-state (dynamic) solution.  $\frac{1}{2}$ 

Therefore,  $\frac{\partial C}{\partial t}$  equals zero at steady-state conditions, and Eq. (2) reduces to,

$$v_z \frac{\partial C}{\partial z} = R(C) \tag{3}$$

The solution of this equation depends on the reaction kinetics of THMs formation. For THMs formation in the pipe network, R(C) is assumed to be first-order growth limited reaction, the growth is limited to THMs formation potential ( $C_{\text{FP}}$ ) of the source water which is the limiting concentration to which THMS can grow.

$$R(C) = k(C_{\rm FP} - C) \tag{4}$$

and Eq. (3) becomes:

$$v_z \frac{\partial C}{\partial z} = k(C_{\rm FP} - C) \tag{5}$$

which gives the following solution,

$$C = C_{0,\text{THM}}[C_{\text{FP}} - C_{0,\text{THM}}][1 - \exp(-kt)]$$

$$t = \Delta z/v_z$$
(6)

where  $C_{o,THM}$  is the initial THMs concentration,  $\Delta z$  is the length of a segment, and  $v_z$  is the average flow velocity in the segment.

Now, pipes of various sizes in a network are connected at junctions or nodes. Under the assumption that the flows of a constituent entering and outgoing at a junction mix completely and instantaneously; junction nodes are modeled as mixed flow reactors with negligible residence (retention) time.

The concentration equation for junction can be written as:

$$C_{\rm nj} = \frac{\sum_{i=1}^{Np} Q_i C_i}{\sum_{i=1}^{Np} Q_i} \quad (j = 1, \dots, Nn)$$
(7)

where  $Q_i$  is the flow rate in *i*<sup>th</sup> pipe section entering that node,  $C_i$  the downstream concentration pipe entering the node, and Np is number of pipes that input to nodes.

If the concentrations at each node and at both ends of each pipe segment are known, then (2Np + Nn) equations are needed to be solved for the unknowns, where Np is number of pipes and Nn is number of nodes in the network. These equations are:

# (1) Steady-state solution:

For THMs formation, Eq. (6) is applied to each pipe segment as follow:

$$C_{i+1} = C_i + [C_{FP} - C_i](1 - \exp(-k\Delta t_i)), \quad (i = 1, ..., Np)$$
  
(8)

where  $C_{i+1}$  is downstream concentration of pipe segment *i*,  $C_i$  is upstream concentration of pipe segment *i*, *k* is first-order growth constant, and  $\Delta t_i$  is the time step required to travel from one end to the other in the *i*th pipe segment. So, Eq. (8) will result in *Np* equations.

(2) The upstream concentration of pipe equals the concentration of the upstream node or the source for the first section.

$$C_{i} = C_{nj}, \left\{ \begin{array}{l} i = 1, \dots, Np \\ j = 1, \dots, Nn \end{array} \right\}$$
 (9)

where  $C_{nj}$  is the concentration at node *j* and Eq. (9) will result in *Np* equations.

(3) Eq. (7) is applied to each node in the network. This gives Nn equation.

Now, the total number of equations is (2Np + Nn) equations which can be linearized and solved, assuming that each pipe contains one segment.

The unsteady-state one-dimensional convective equation is a parabolic differential equation which can be solved using a numerical technique employing an implicit finite-difference scheme, in which the partial derivatives and/ or the coefficients are replaced in terms of the values at the unknown time level. The unknown variables appear implicitly in the algebraic equations that have to be solved simultaneously in these methods [10].

The method used is known as Preissman scheme which has been used to solve for unsteady open-channel flow problems with steep wave front. Steep wave fronts may be properly simulated by varying the weighting coefficient; the scheme yields an exact solution of the linearized form of the governing equations for particular value of  $\Delta z$  and  $\Delta t$ .

Most finite difference schemes introduce an unwanted numerical diffusion for the convective term when partial derivatives are discretized with Taylor series.

The generation of numerical diffusion is illustrated using Taylor series expansion as follows:

$$\frac{\partial C}{\partial t}\Big|_{(i+1,n+1)} + v\frac{\partial C}{\partial z}\Big|_{(i+1,n+1)} = 0$$
(10)

Therefore, if a first-order accurate difference is used to approximate both derivatives, Eq. (10) can be written as:

$$\frac{C_{i+1}^{n+1} - C_{i+1}^{n}}{\Delta t} + v \frac{C_{i+1}^{u} - C_{i}^{n}}{\Delta z} = 0$$
(11)

Using and substituting Taylor series expansion into Eq. (11), and then differenting it with respect to t, and rearranging yields:

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial z} + \left( v^2 \frac{\Delta t}{2} - v \frac{\Delta z}{2} \right) \frac{\partial^2 C}{\partial z} = 0$$
(12)

As shown in Eq. (12), a new numerical term is introduced which is  $\left[v^2 \frac{\Delta t}{2} - v \frac{\Delta z}{2}\right] \frac{\partial^2 C}{\partial z^2}$  this term is called numerical diffusion term which is similar to the molecular diffusion term. Avoiding such a numerical diffusion term involves finding the conditions that make this term equal to zero.

i.e.

$$\left[v^2\frac{\Delta t}{2} - v\frac{\Delta z}{2}\right]\frac{\partial^2 C}{\partial z^2} = 0$$

It can be shown that this is acheived when the following condition is met:

$$v\Delta t = \Delta z$$
 or  $v\frac{\Delta t}{\Delta z} = 1$   
 $v\frac{\Delta t}{\Delta z} = 1$  is known as Courant number:  $\alpha = v\frac{\Delta t}{\Delta z}$ 

The partial derivatives and other coefficients of Eq. (12) are approximated as follows:

$$\frac{\partial C}{\partial t}\Big|_{(i+1,n+1)} \cong \psi \frac{C_i^{n+1} - C_i^n}{\Delta t} + (1-\psi) \frac{C_{i+1}^{n+1} - C_{i+1}^n}{\Delta t}$$
(13)

$$\frac{\partial C}{\partial z}\Big|_{(i+1,n+1)} \cong (1-\theta) \frac{C_{i}^{n+1} - C_{i}^{n}}{\Delta z} + (1-\psi) \frac{C_{i+1}^{n+1} - C_{i+1}^{n}}{\Delta z}$$
(14)

$$C \cong \psi \left[ \theta C_{i+1}^{n+1} + (1-\theta)C_i^n \right] + (1-\psi) \left[ \theta C_i^{n+1} + (1-\theta)C_{i+1}^n \right]$$
(15)

in which  $\theta$ ,  $\psi$  are weighting coefficients (in the temporal and spatial dimensions, respectively).

Now, the solution for the unsteady-state THMs formation is obtained by substituting Eqs. (4), (13)–(15) in Eq. (4), and upon rearrangement the following equation is obtained:

$$a_0 + a_1 C_{i+1}^{n+1} + a_2 C_i^{n+1} + a_3 C_{i+1}^n + a_4 C_i^n = 0$$
(16)

where,

$$a_{0} = -k\Delta t C_{FP}$$

$$a_{1} = (1 - \psi) + \alpha \theta + k\Delta t \psi \theta$$

$$a_{2} = \psi - \alpha \theta + k\Delta t \theta (1 - \psi)$$

$$a_{3} = -(1 - \psi) + \alpha (1 - \theta) + k(1 - \psi)(1 - \theta)\Delta t$$

$$a_{4} = -\psi - \alpha (1 - \theta) + k\Delta t \psi (1 - \theta)$$

Eqs. (7), (9), and (16) are used to solve for unsteadystate THMs formation concentrations in the network.

To sum up, if a water distribution system composed of a network consisting of Np pipes that are divided into Ns segments and Nn nodes, then the number of unknowns is [(Ns + 1) Np] + Nn. Therefore, [(Ns + 1) Np] + Nn equations are needed for each time step.

These equation are obtained as follows:

- Eq. (16), for THMs concentration, gives (*NsNp*) equations.
- The upstream concentrations in a pipe equals the concentrations of the upstream nodes, and hence Eq. (9) gives *Np* equations.
- Eq. (7), which is applied to each node in the water distribution network, gives *Nn* equations.
- This procedure is applied for every time step, and at each time step
- (*Ns* + 1) *Np* + *Nn* equations are linearized and solved until the simulation is done.

## 4. Model simulation

The true test of simulation model is the successful application to a real distribution system. Hence, Table 2 summarizes the border conditions of the model simulation. The dynamic simulation time was taken as 106 h and the travel (retention) time for each pipe was determined from the length of the pipe divided by the flow velocity in the pipe. The time step was taken as 3 min which is equal to or less than the travel time in the pipe that had the maximum velocity in the network. The first-order THMs formation rate constant of  $5.82 \times 10^{-2}$ /h was used.

Values of  $\psi$  and  $\theta$  were assumed to be 0.5 and 0.6, respectively; since the model is stable for the following conditions:

```
 \begin{split} \psi &= \theta \quad 0 \leq \psi \leq 1 \\ 0 \leq \theta \leq 1 \\ \psi &\neq \theta \quad 0 \leq \psi \leq 1 \\ 0.5 \leq \theta \leq 1 \end{split}
```

As for the Courant number ( $\alpha$ ), its value may influence the model's results and stability. As  $\alpha$  value decreases below 1; a molecular diffusion term will be introduced by the numerical scheme causing an increase in THMs concentration, and when it approaches a very low value; ( $0 < \alpha \le 0.05$ ) the model

 Table 2

 The border conditions of the model simulation

Condition	Value
Initial TTHMs	112.87 pbb
TTHMs <sub>FP</sub>	*
THMs formation rate constant	$5.82 \times 10^{-2}/h$
Dynamic simulation time	106 h
Time step	3 min
ψ	0.5
$\theta$	0.6
Courant number ( $\alpha$ )	1

will be unstable. Value of 1 is taken for the Courant number in this model because it fits the experimental data better than other values.

The demand pattern (network flow rates) are determined for each pipe in the network based on the daily water demand consumption; assuming that 80 liters/ capita is the maximum water demand per day. Thus, the pipe maximum flow rate is equal to the total population water demand, who is served by that pipe at different time intervals in each day (i.e. water demands in morning is different than that at night).

Flows in the network were aggregated into fivetime periods in each day, ranging in length from 4 to 6 h, during which flows throughout the system remained relatively constant. These flow intervals were input into the dynamic water quality model as a percentage of the original maximum flow rate.

### 5. Results and discussions

#### 5.1. Kinetics of THMs formation and chlorine decay

The kinetics of THMs formation and chlorine decay of the treated water samples taken from the effluent water of Zai water treatment plant are shown in Fig. 4. The THMs measurements chromatograms for initial time and THMs potential formation (after 7 d) are shown in Fig. 5.

The kinetics of THMs formation and chlorine decay in bulk phase which were determined in this study are compatible with each other, since both of them present similar first-order behavior (growth and decay, respectively), and after 23h the decay rate of chlorine is equal to THMs growth rate. THMs formation and chlorine decay behaviors were quite fast at the beginning and it is apparent from the curves that quite rapid and slow reactions were taking place.

The first-order limited THMs growth rate constants were determined for the various species using available fitting techniques, and tabulated in Table 3. The growth rate constant for the THMs formation was compared with other experimental data in the literature and found to be within the range for similar initial and THMs formation potential values [12].

The first-order chlorine decay rate constant was determined and found to be  $0.53 d^{-1}$ . The experimental decay rate obtained in this study was in very close agreement with other studies. A bulk decay constant of  $0.5 d^{-1}$  and  $0.55 d^{-1}$  was reported by Clark and Rossman [8,13,14].

The quality of the water samples taken from the field network, at the three sampling points, was characterized in terms of the factors that are influencing



Fig. 4. THMs formation and chlorine decay relationship.



Fig. 5. THMs measurements chromatograms for (a) initial time (b) THMs formation (after 49.25h).

the total trihalomethanes (TTHMs) formation and variation in the distribution system as shown in Table 4.

The modeled results for THMs formation in the field network were compared favorably with the

observed data for three sampling points in the network. Fig. 6 compares the predicted and observed means at the three sampling points. The correlation coefficient between the two is 0.9164. Table 3

Kinetic data of THMs formation at temperature 16°C, pH 7.8, TOC 1.14 ppm, initial free chlorine 1.04 ppm, and bromide ion 0.42 ppb

Formula	$C_{\rm o}$ (µg/l)	$C_{\rm FP}$ (µg/l)	$k (h^{-1})$
TTHMs	18.29	97.89	$5.82 \times 10^{-2}$
CHCL <sub>3</sub>	0.12	0.51	_
CHBrCL <sub>2</sub>	0.73	2.70	$2.32 \times 10^{-2}$
CHBr <sub>2</sub> CL	4.90	16.07	$3.65 \times 10^{-2}$
CHBr <sub>3</sub>	12.49	78.60	$2.29\times10^{-2}$

Table 4

Average water quality characteristics at the three sampling points

Water characteristic	Value
Temperature range	10–18℃
pH	7.86
Free chlorine	0.55 ppm
TOC	$\cong 1.14 \text{ ppm}$
Bromide Ion	0.42-0.5 pbb
TTHMs (at source point)	112.87 pbb
TTHMs (formation potential at lab scale)	141.445 pbb

The THMs formed inside the selected network of this case study were sixfolds higher than that formed in Zai treatment plant (18.3 ppb); and 113% higher than that average value formed in Kharabshe Reservoir (111 ppb). The formation of THMs in the water network is influenced by the source THMs concentration, when the water level in reservoir decreases below the required level, fresh water with



Fig. 6. Modeled and observed THMs means at the three sampling points.

different quality is pumped into the reservoir to substitute the shortage in the water level. As a result of that, the THMs in the source node (reservoir) are changed and this affects the THMs formation in the distribution system specially sampling point (1) since it is the closest point to the reservoir. This is shown in Figs. 7–9 for the three sampling points, respectively.

Moreover, an investigation was made on the effect of the distance between the sampling points and water from the same reservoir on the levels of THMs. This is because it was not possible to use tracers to measure retention times in the system. Figs. 7 and 9 show that at the points chosen, it was possible to establish a relationship between the levels of THMs and distance. Accordingly, the variation in THMs concentrations is clearly appeared in sampling point (3) more than sampling point (1). However, one should not ignore the fact that whenever there is greater water demand (for instance, a much more heavily populated area), implying a lower retention time in the network at that point, then the THMs formation will be less regardless of the location of the sampling point. Sampling point 2 is a good example of this special case as shown in Fig. 8.

Water demand is one of the water quality model key inputs. Thus, at peak hours, when consumption is high (e.g. from morning to late afternoon), as shown



Fig. 7. THMs variation at sampling point (1).



Fig. 8. THMs variation at sampling point (2).



Fig. 9. THMs variation at sampling point (3).

in Figs. 10–12, the water transits more rapidly to the network pipes and this influences the kinetics of THMs formation since the free chlorine has not enough time to react with the humic substances; thus the change in THMs concentration values is gradually pronounced. However, when consumption is low at off-peak hours (e.g. during the night), water velocity decreases and the THMs formation values are more pronounced. For sampling points 1 and 2 in the selected water distribution network, all THMs values computed during the last two days of the simulation remain greater than the minimum admissible range, which is 120–130 ppb.

As stated before, courant number ( $\alpha$ ) value may influence the model's results and stability, and this is



Fig. 10. Flow rate variation at sampling point (1).



Fig. 11. Flow rate variation at sampling point (2).



Fig. 12. Flow rate variation at sampling point (3).



Fig. 13. Effect of courant number (alpha) on THMs at sampling point (1).

shown in Fig. 13. As  $\alpha$  value decreases below 1; a molecular diffusion term will be introduced by the numerical scheme causing an increase in THMs concentration, and when it approaches a very low value; ( $0 < \alpha \le 0.05$ ) the model will be unstable. Value of 1 is taken for the courant number in this model because it favorably fits the experimental data more than other values.

# 6. Conclusions

Reaction kinetics for THMs and chlorine in the bulk fluid were studied by analyzing the results of bottles tests made on drinking waters. THMs formation and chlorine decay kinetics are compatible with each other, since they both present similar first-order behavior.

The THMs formation rate coefficient measured in the bottle test was assumed to accurately represent the rate coefficient for bulk formation in the distribution system. The first-order kinetic model of THMs formation showed an acceptable performance in actual drinking water distribution systems. The increase in THMs formation in drinking water systems depends largely on the concentration of THMs at the source, water demand, and locations of the sampling points. The THMs formed inside the pipelines and distribution systems in this case study were six folds more than that formed in Zai treatment plant; and 113% more than that formed in Kharabshe Reservoir. In conclusion, the model output has shown that it is a suitable method for estimating the THMs concentrations in a water distribution network, and for monitoring health risks associated with THMs in drinking water distribution systems.

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