

Rapid water quality characterization for chlorine demand and THM formation in drinking waters

V. Jegatheesan, S. Weragoda and C. Visvanathan

ABSTRACT

The quality of drinking water generally deteriorates when it is delivered through a distribution system due to the decay of disinfectant, which subsequently allows the re-growth of microorganisms in the distribution system in addition to the formation of trihalomethane (THM). Therefore, a model which describes the changes that occur in the water quality in the distribution system is needed to determine whether to enhance the treatment processes or to improve the distribution system so that microbiological criteria are met. In this paper the chlorine decay kinetics and THM formation in treated water is modeled considering the reaction of chlorine with fast and slow reacting organic and nitrogenous compounds which are present in that water. The treated water was also passed through three types of resins to fractionate very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU) compounds which are present in the water. Chlorine decay tests were conducted on the effluents emerging from the resins to evaluate the chlorine demand and THM formation potential of those organic fractions. The model shows that the CHA presented in the waters has a very high THM formation potential (around 62% of the THM produced). VHA, NEU and CHA contributed to chlorine demand in the water.

Key words | chlorine decay, nitrogenous compounds, organic fractionation, organic/inorganic compounds, THM, water quality modelling

V. Jegatheesan
School of Engineering,
James Cook University,
Townsville, QLD 4811,
Australia

S. Weragoda
C. Visvanathan (corresponding author)
Environmental Engineering and Management
Program,
Asian Institute of Technology,
PO Box 4, Klong Luang,
Pathumthani 12120,
Thailand
Tel/Fax: +61 2 524 5640
E-mail: visu@ait.ac.th

INTRODUCTION

Drinking water starts its journey within catchments, and is subsequently purified at treatment plants and delivered through distribution systems. The water quality generally deteriorates during its passage through the catchment, but the subsequent treatment processes produce water of high quality. However, within distribution systems, the quality of the water generally deteriorates again. A major problem which occurs in distribution systems is the decay of disinfectant. This allows the re-growth of microorganisms in the distribution systems. Trihalomethanes (THMs) are also produced as by-products during chlorine decay. Therefore, a model which describes the changes in the quality of water that occur in distribution systems is needed to determine how much to enhance the treatment processes (by modifying the existing processes or adding advanced processes to the existing system) or to

improve distribution systems so that microbiological criteria are met. Improvement of a distribution system can be in several forms, such as installing re-chlorination stations and cleaning mains or service reservoirs etc.

History of the modelling of chlorine decay in piped water dates back to 1950 (Table 1). Chlorine decay does not take place at all in pure water in the dark which indicates that chlorine is reacting with some impurities present in natural waters rather than decomposing on its own. Experiments indicate that reaction rate coefficient is a function of the initial chlorine dose and amount of chlorine already reacted with this particular water. The first order approximation is based on the assumption that chlorine reacts with contaminants in water, which are presented in much larger quantities than chlorine. Therefore the concentration of the contaminants is not

doi: 10.2166/aqua.2008.043

Table 1 | Summary of the chlorine decay and DBPs formation models

Model	Notation	Description	Reference
$C_{av} = e^{(-A_1X)/(1 + \varepsilon)}$	All parameters are dimensionless. C_{av} -Cup mixing average concentration A_1 -Constant X -Axial distance ε -Fractional error	This model is developed to find the average chlorine concentration in pipes. A generalized expression for Cl consumption at the pipe wall is used to solve the equation.	Biswas <i>et al.</i> (1993)
$k_b = e(\text{TOC}-f)$	k_b -Bulk first order chlorine decay constant (1/h), TOC-total organic carbon concentration (mg/L) f -TOC for zero k_b (mg/L) e -Slope of k_b against TOC (mg/L h).	The 1st equation describes decay constant is adversely proportional to the TOC content.	Powel <i>et al.</i> (2000)
$k_b = m/C_o$	C_o -Initial chlorine concentration (mg/L), m -Slope of k_b against $1/C_o$ (mg/L h).	The 2nd equation describes that the decay constant is inversely proportional to the initial concentration of chlorine.	
$(1/C) + (k_2/k_1) = (1/C_o + k_2/k_1)e^{k_1t}$	C -Chlorine concentration at time t (mg/L) C_o -Initial chlorine concentration (mg/L), T -Time (h) k_1 -Decay constant (1/h) k_2 -Decay constant (L mg ⁻¹ h ⁻¹)	This model expresses that combined 1st and 2nd order model is better than simple 1st order model to describe the variation of Cl decay.	Hua <i>et al.</i> (1999)
$\text{TTHM} = T\{C_{AO} - [C_{AO}(1 - R)/(1 - \text{Re}^{-ut})]\} + M$	T -Dimensionless parameter C_{AO} -Initial chlorine residual of A (mg/L) C_{BO} -Initial chlorine residual of B (mg/L) a -Coefficient of reacting substance A b -Coefficient of reacting substance B M -Estimated value of TTHM at time zero (mg/L) k_A -Reaction rate constant for formation of A	This model describes Cl decay and THM formation with the help of 2nd order kinetics.	Clark (1998)
$R = (aC_{BO}/bC_{AO}) \quad u = (bC_{AO}/a - C_{BO}) \times k_A,$			
$C_{cup} = \{ \int_0^1 2\pi RCdR \} / \{ \int_0^1 2\pi RdR \}$	C_{cup} -Dimensionless average chlorine concentration of the pipe at any cross-section R -Dimensionless radial distance from pipe center C -Dimensionless point value of chlorine concentration in the cross-section.	This model provides the average Cl concentration at any cross-section. The model accounts for axial convection and radial diffusion in a pipe under turbulent, transitional and laminar flow regimes and uses realistic velocity profiles.	Ozdemir & Ger (1998).

Table 1 | (continued)

Model	Notation	Description	Reference
$-d[\text{Cl}]/dt _{\text{cor}} = (M_{\text{Cl}_2}/F_d) \times i_{\text{cor}}$	M_{Cl_2} -Cl ₂ molar weight i_{cor} -Corrosion current density	This model can be used to find the Cl consumption for corrosion.	Fraturet <i>et al.</i> (1999).
$\text{THM}_t = \text{THM}_o \exp(kt)$	k -Rate constant	This model can be used to predict the concentration of THM in the transporting pipelines.	Shafy & Grunwald (2000).
$-d[\text{NH}_2\text{Cl}]/dt = 3k_{\text{Br}}K[\text{NH}_2\text{Cl}][\text{Br}^-][\text{H}^+] + 2k_{\text{HOCl}}[\text{HOCl}][\text{Br}^-]$	k -Rate constant	This model consists of encompassing auto decomposition as well as reactions with nitrite and bromide.	Vikesland <i>et al.</i> (2001).
$\text{TTHM} = 0.00253(\text{DOC})^{1.22}(\text{Cl}_2)^{0.442}(\text{pH})^{1.75}(t)^{0.54}(\text{temp})^{1.514}$	TTHM-Total trihalomethane	DOC based model for raw water(developed from EPA 1987 database)	Sohn <i>et al.</i> (2004)
$C_t = C_o \times (1 - K \times C_r/D \times t)$	C_o, C_t -Cl concentration C_r -Water velocity in microm/year	This model gives the Cl demand due to corrosion process.	Kiene <i>et al.</i> (1998)
$\text{TTHM} = 10^{-1.385}(\text{DOC})^{1.098}(\text{Cl}_2)^{0.152}(\text{Br}^-)^{0.068}(\text{temp})^{0.609}(\text{pH})^{1.601}(\text{time})^{0.263}$	DOC-Dissolved organic carbon	DOC- based model for THM formation and applicable for raw water.	Sohn <i>et al.</i> (2004)
$\text{TTHM} = 0.42(\text{UVA})^{0.482}(\text{Cl}_2)^{0.539}(\text{Br}^-)^{0.023}(\text{temp})^{0.617}(\text{pH})^{1.609}(\text{time})^{0.261}$	UVA-Ultraviolet absorbance	UVA- based model for THM formation and applicable for raw water.	Sohn <i>et al.</i> (2004)
$\text{TTHM} = 0.283(\text{DOC}^* \text{UVA})^{0.421}(\text{Cl}_2)^{0.145}(\text{Br}^-)^{0.041}(\text{temp})^{0.614}(\text{pH})^{1.606}(\text{time})^{0.261}$		UVA*DOC- based model for THM formation and applicable for raw water.	Sohn <i>et al.</i> (2004)
$\text{TTHM} = 3.296(\text{DOC})^{0.801}(\text{Cl}_2)^{0.261}(\text{Br}^-)^{0.223}(\text{time})^{0.264}$		DOC- based model for THM formation and applicable for coagulated water	Sohn <i>et al.</i> (2004)
$\text{TTHM} = 75.7(\text{UVA})^{0.593}(\text{Cl}_2)^{0.332}(\text{Br}^-)^{0.060}(\text{time})^{0.264}$		UVA- based model for THM formation and applicable for coagulated water	Sohn <i>et al.</i> (2004)
$(dC_A/dt) = k_1 C_A + k_2 C_A^2$	a, b -stoichiometric coefficients for describing the fictive reaction mechanism	The model can be applicable for the re-chlorination conditions	Boccelli <i>et al.</i> (2003)

Table 1 | (continued)

Model	Notation	Description	Reference
Where $k_1 = \frac{b}{a}k_A C_{A,0} - k_A C_{B,0}$ and $k_2 = -k_A \frac{b}{a}$ $TTHM = T(C_{A_0} - [C_{A_0}(1 - R)/(1 - Re^{-ut})])$	k_A -second order Cl decay coefficient C_A -Cl concentration of the fictive reaction C_B -fictive reactant concentration of the fictive reaction T -dimensionless parameter C_{A_0} -initial Cl residual (mg/L) R -dimensionless parameter from the Cl decay equation u -the reaction rate constant	TTHM formation based on chlorine consumption	Clark (1998)

significantly changed during the reaction with chlorine and the reaction rate is only proportional to the chlorine. The main advantage of this type of pseudo-first order reaction scheme is its simplicity and the available analytical solution, with no need to keep track of any other concentrations but chlorine (Kastl *et al.* 1999). However, this is not correct as the demand of chlorine will be based on the concentrations of contaminants which consume chlorine and the estimation of the concentration of remaining contaminants is essential to predict the total and immediate chlorine demand accurately. In this sense, the existing models are not sufficient.

In this paper the chlorine decay kinetics and THM formation are modelled to compare the chlorine demand in treated water. This model can estimate the magnitude of fast and slow reducing (organic and inorganic) compounds and nitrogenous compounds present in the water which consumes chlorine as well as the THM formation in the water due to the reaction between chlorine and the fast/slow reacting compounds (the common inorganic substances in the water are Fe^{2+} , Mn^{2+} and H_2S , which will mostly be removed by treatment plants through aeration). The model also estimates the reaction rates of those compounds when they react with chlorine. Thus, the model will be able to predict the initial chlorine demand (due to its interaction with fast reducing organic/inorganic and nitrogenous compounds) and the continuing demand (due to the interaction of chlorine with slow reducing organic/inorganic and nitrogenous compounds) for raw or treated water. The model prediction of initial chlorine demand of the treated water and the actual initial chlorine demand at the treatment plant could be used in finding the elements which are contributing to the consumption of chlorine at the treatment plant other than the water itself (such as pumps and pipes at the treatment plant); this allows better control of chlorine dosing at the treatment plant, which in turn will reduce the formation of disinfection by-products (DBPs). In addition the model will accurately predict the decay due to the organic/inorganic and nitrogenous compounds which are remaining in the water at any point in the distribution system, if the travel time of water to the point from the treatment plant is known. Thus, the difference between the chlorine level predicted by the model and the actual chlorine level at the point will indicate the status of the distribution system with respect

to its chlorine consumption (due to biofilm and corrosion). Further, if re-chlorination is introduced in the distribution system downstream of the treatment plant the model will predict the chlorine decay due to the slow reacting organic/inorganic and nitrogenous compounds accurately.

Further, rapid organic characterization of the water was carried out to estimate the different organic fractions which are present in the water as well as their chlorine demand and THM formation potentials. The treated water was passed through three types of resins to fractionate very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU) compounds which are present in the water. Chlorine decay tests were conducted on the effluents emerging from the resins to evaluate the chlorine demand and THM formation potential of those organic fractions. In this study, the THM formation potential of the treated and treated/-fractionated waters is evaluated by measuring the THM of those samples.

STUDY LOCATION

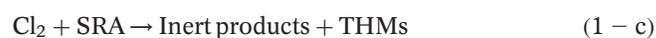
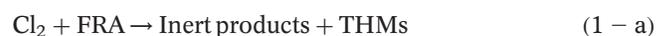
The research was carried out on treated water from Bangkhen water treatment plant, located in Bangkok, Thailand. Water from Chao Praya River is used as the raw water source for this treatment plant.

The Bangkhen water treatment plant consists of 16 units of solid contact clarifiers with a capacity of 200,000 m³/d per unit and 44 units of rapid sand filters with a capacity of 75,000 m³/d per unit. The maximum capacity of the plant is 3.2 million m³/d. The clarifiers are designed based on the concept of slurry circulation and the size of one clarifier is 58 m in diameter. The tank is divided into two zones, namely, reaction and sedimentation zones. Pre-lime feeding of 5–15 mg L⁻¹ and 20–70 mg L⁻¹ of alum dose are added to the influent channel of the clarifier. In addition to that, polyelectrolyte of 0.03–0.10 mg L⁻¹ is added to the reaction zone. Filters in Bangkhen water treatment plant have been designed with dual media. These dual media filters consist of 0.8 m anthracite coal as the top layer and 0.4 m graded sand as the bottom layer. The time of one filter run is about 48 hours.

MODELLING

Rapid assessment of chlorine consuming substances in source and drinking waters will provide information on the performance of a water treatment plant as well the quality of the treated drinking water. In order to carry out the assessment, an efficient chlorine decay model is required. The model should be able to predict the initial rapid decay as well the slow continuing decay of chlorine in the test waters. A model considering the initial rapid decay due to fast reducing agents (FRA) such as inorganic and organic compounds as well as fast reducing nitrogenous compounds (FRN) and the continuing slow decay due to slow reducing agents (SRA) and slow reducing nitrogenous compounds (SRN) is used in this study (Kastl *et al.* 1999, 2003) to model the chlorine decay in treated and treated/fractionated waters. The model is capable of providing quantitative initial concentrations (mg L⁻¹ chlorine equivalent) of FRA, FNA, SRA and SNA of the test waters. Thus, the sum of the concentrations of FRA and FNA will indicate the initial chlorine demand and the sum of all four components will indicate the final chlorine demand of the test waters. Also, the model had been validated in previous studies (Kastl *et al.* 1999, 2003) and has been applied for various waters in Australia and Korea to provide rapid characterization of the quality of those waters (Jegatheesan *et al.* 2006).

The chlorine decay data obtained were analysed with AQUASIM (Reichert 1994; Wanner & Reichert 1996) to estimate initial concentrations of organic/inorganic compounds and nitrogenous compounds along with reaction rate constant values. The following reaction schemes were used to model the chlorine decay in the water (Kastl *et al.* 1999, 2003):



$$\text{Cl}_2 + \text{CC} = \text{TC} \quad (1 - f)$$

While Cl_2 indicates the available free chlorine present in the water and the sum of Cl_2 and combined chlorine (CC) indicates the total chlorine (TC) present in the water. The reaction rates for the above five equations are k_1, k_2, k_3, k_4 and k_5 respectively. Also, it is assumed that a fraction of chlorine which reacts with FRA and SRA would form THM. Thus the equations governing the decay of free and combined chlorine and the formation of THM can be written as:

$$\frac{d[\text{Cl}_2]}{dt} = -k_1[\text{Cl}_2][\text{FRA}] - k_2[\text{Cl}_2][\text{FRN}] - k_3[\text{Cl}_2] \times [\text{SRA}] - k_4[\text{Cl}_2][\text{SRN}] \quad (2 - a)$$

$$\frac{d[\text{CC}]}{dt} = -k_5[\text{CC}] + k_2[\text{Cl}_2][\text{FRN}] + k_4[\text{Cl}_2][\text{SRN}] \quad (2 - b)$$

$$[\text{Total Cl}_2] = [\text{Cl}_2] + [\text{CC}] \quad (2 - c)$$

$$\frac{d[\text{THM}]}{dt} = \alpha k_1[\text{Cl}_2][\text{FRA}] + \beta k_3[\text{Cl}_2][\text{SRA}] \quad (2 - d)$$

where α and β are the THM formation coefficients. These processes were constructed in AQUASIM, which contains a dynamic equation solver which can perform parameter estimation to find the best fit of the model output to the experimental data (Reichert 1994). In this study the experimental chlorine decay data were used to estimate the initial concentrations of fast and slow reducing organic/inorganic and nitrogenous compounds along with the reaction rates k_1 through k_5 ; and THM concentration data were used to estimate α and β . The weighted error between experimental and model (χ^2) data can be used as a measure of goodness of fit of the model to the experimental data. The weighted error, χ^2 is defined as:

$$\chi^2(\mathbf{p}) = \sum_{i=1}^n \left[\frac{f_{\text{meas},i} - f_i(\mathbf{p})}{\sigma_{\text{meas},i}} \right]^2 \quad (3)$$

where: $f_{\text{meas},i}$ is the i th measured value, $f_i(\mathbf{p})$ is the calculated value from the model, using parameter values \mathbf{p} and $\sigma_{\text{meas},i}$ is the estimated standard deviation of $f_{\text{meas},i}$. During the fitting of the model to the experimental data, the initial concentrations of fast and slow reducing organic/inorganic and nitrogenous compounds along with

the reaction rates k_1 through k_5 were adjusted by the AQUASIM software until χ^2 reached a minimum value. The initial concentrations of FRA, FRN, SRA and SRN were obtained as mg L^{-1} of chlorine equivalent. Once the above parameters have been estimated, fitting the THM formation model to the experimental data was carried out to estimate α and β in a similar manner.

TECHNIQUE ON RAPID ORGANIC CHARACTERIZATION

Natural organic matter (NOM) is used to describe the complex mixture of organic material present in all drinking water sources such as humic acids, hydrophilic acids, proteins, lipids, amino acids and hydrocarbons. The variety of the components in NOM changes from water to water which leads to variations in the reactivity with chemical disinfectants such as chlorine, ozone and chlorine dioxide. The understanding of the structure and abundance of these components is therefore vital in the understanding of how to predict and control DBPs in water treatment processes.

The rapid characterization technique, presented in Figure 1, was based upon the full scale fractionation scheme reported by Bolto *et al.* (1999) for determination of the concentration of four organic fractions namely, very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU) compounds. The rapid organic characterization technique basically depends on the fractionation by non-functionalised resins (DAX-8 and XAD-4) and an anion exchanger (IRA-958), and characterized by size exclusion chromatography. The summary of fractionation by those resins is shown below (Chow 2004):

- VHA = Raw water – (DAX-8 effluent)
- SHA = (DAX-8 effluent) – (XAD-4 effluent)
- CHA = (XAD-4 effluent) – (IRA-958 effluent)
- NEU = (IRA-958 effluent)

The resins DAX-8, XAD-4, and IRA-958 can also be used in the water treatment plants with the application of alum as coagulant to remove organic matter. This will reduce the excessive true colour of water and reduce the formation of DBPs during disinfection.

The above fractionation technique is rapid, allowing the water treatment operators to react quickly when changes to raw water quality occurs or to use the results to fine-tune the treatment processes. With the ability to determine organic fraction concentrations in treated waters, the application of this technique can be extended to study the link between the organic fractions and their potentials to form disinfection by-products.

MATERIALS AND METHODS

Water samples of 20 L in volume were collected from the water treatment plant, prior to the post chlorination. Samples were collected in polyethylene cans. These cans were prepared for sampling by washing them first with detergent and then with the chromic acid washing solution. Then they were rinsed thoroughly with tap water followed by distilled water. Samples were dechlorinated using sodium bisulphite (NaHSO_3) in order to measure the total Organic Carbon (TOC) in the samples. NaHSO_3 solution was prepared by dissolving 2.931 g of NaHSO_3 powder in 1 L of deionised water to have a concentration such that 1 mg of chlorine can be

de-chlorinated with 1 ml of NaHSO_3 solution. Collected samples were always stored under the controlled temperature of 5°C . The rapid organic characterization technique presented in Figure 1 was used to differentiate the dissolved organic compounds into four fractions.

The water samples of 2 L, collected from each column, were chlorinated with sodium hypochlorite stock solution (1 mg/ml) to produce an initial chlorine dose of 3 mg L^{-1} (the initial dosing of chlorine was maintained at a level which is similar to the one applied in the water treatment plant). Generally the pH of the solution after the addition of sodium hypochlorite was around 7.0 where the predominant species of chlorine are HOCl and OCl⁻ and both contribute to the free chlorine concentration. The ratio of HOCl to OCl⁻ at pH 7.0 and 25°C is 3.17 (Snoeyink & Jenkins 1980). Free and total chlorine readings were taken immediately after dosing to find the initial chlorine demand. Further, these two parameters were observed at intervals of 5, 10, 20, 30 minutes and 1, 2, 4, 6 hours and so on until the chlorine concentration becomes negligible (below 0.2 mg L^{-1}). Chlorine concentrations were determined using the DPD colorimetric method, by dissolving DPD (N, N-diethyl-p-phenylenediamine) indicator in

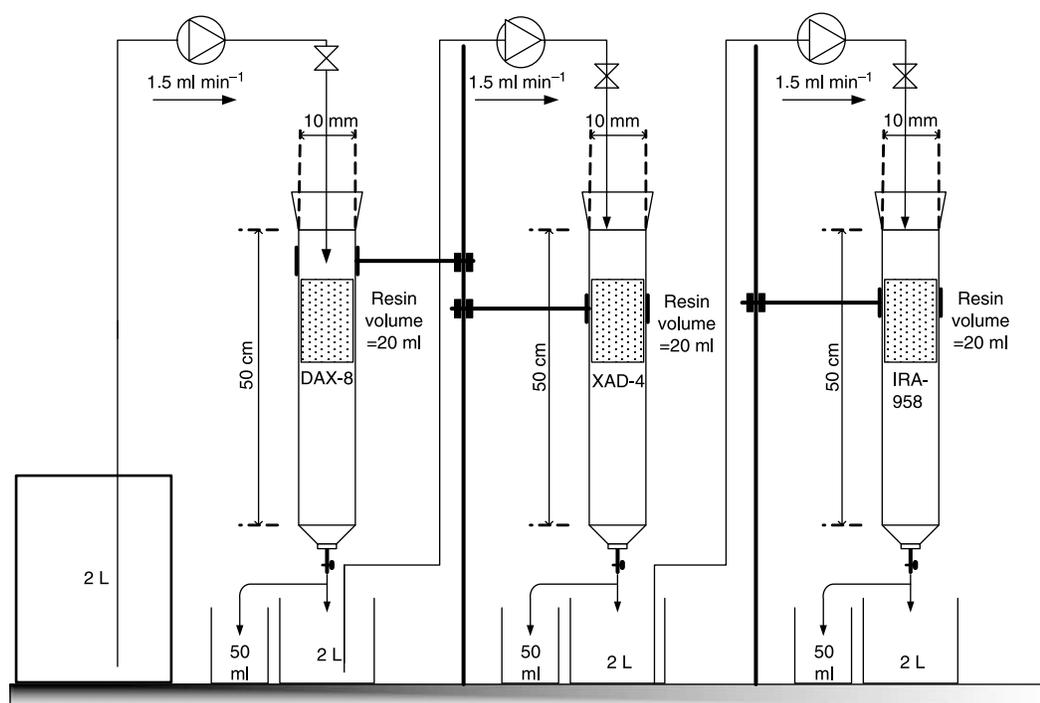


Figure 1 | Experimental set up for rapid organic characterization.

25 ml of sample as explained in the standard methods for the examination of water and wastewater (*Standard Methods 1995*) and measuring the color developed by a HACH pocket colorimeter. In addition to that, the experiments were carried out at a control temperature of 25°C. Again if we consider the conditions at which the experiments have been conducted (25°C and pH of 7.0), the volatilization of chlorine becomes negligible above pH 2.0. Therefore volatilization has not been included in the study. Further, the chlorine decay experiments were conducted in dark bottles which were kept out of sunlight with the lids on. Thus, the chlorine loss due to volatilization and reaction with sunlight are negligible. The sodium hypochlorite stock solution was stored in a volumetric flask (covered with aluminum foil) in the refrigerator under 5°C for further dosing of water samples.

THM formation was also measured for each sample which was obtained from the columns and chlorinated. A special procedure was followed for the preparation of 50 ml bottles, which were used to store samples for THM analysis. These bottles were first washed with tap water and then chromic acid. Again, they were washed with tap water and then followed by DI water. After washing several times, the bottles were kept in an oven at a controlled temperature of 150°C for 1 hour.

THM determination was carried out in two steps: separation and analysis of concentrations. Separation was carried out by using the liquid-liquid separation technique, where the organic solvent pentane was used as described in the standard methods for the examination of water and wastewater (*Standard Methods 1995*). The analysis was carried out using a gas chromatograph with the following specifications: Model - HP 5890 series II (Helwett Packard), Detector used: Electron capture Detector (ECD), Column: Capillary (HP-5), 30 m × ID 0.32 mm × Film thickness 0.25 μm, Function - Determination of Chlorinated Organic Compounds.

A UV-160 spectrophotometer was used to measure the absorbance values of each water sample at 254 nm wavelength. These values represent the presence of conjugated double bonds in dissolved organic compounds. The UV-160 spectrophotometer has the following specifications: Double beam UV-VIS Spectrophotometer, Shimadzu, Japan, Model - UV 160A.

A TOC analyser with the following specifications was used to measure the dissolved organic carbon concentration

in the water samples. Model - Shimadzu, TOC -5000A, Application: liquid, Analytes: TC, IC, TOC(TC - IC), Method: combustion, Combustion temperature: 680°C, measuring range: <20 mg L⁻¹, Sample introduction: automatic injection, sample injection volume: 50 ~ 2,000 μL.

RESULTS AND DISCUSSION

Water treatment plant

Raw water quality and pre-chlorination

The raw water quality data of Chao Praya River are presented in the [Table 2](#). The pre-chlorination is carried out with an initial chlorine dose of 2 mg L⁻¹ to prevent the growth of algae, which may interfere with the treatment of water and cause taste and odour problems. [Figure 2](#) presents the chlorine decay patterns observed in the treatment plant. The highest chlorine decay was observed in between the hydraulic jump and the clarifier. This was due to fast mixing of chlorine with water and reacting with the fast reducing organic and inorganic compounds in the raw water. Therefore the rest of the plant did not have any significant effect from chlorine until the post chlorination is applied.

Water distribution system

Bangkhen water distribution system

In order to analyze chlorine decay and THM formation in the distribution system of Bangkhen water treatment plant, one of the most far away reservoirs, which is located about

Table 2 | Raw water quality data of Chao Praya River

Parameter	Unit	Average	Maximum	Minimum
Temperature	°C	29.5	30.8	28.1
Turbidity	NTU	91	149	50
Colour	Pt-Co unit	40	50	30
BOD	mg L ⁻¹	<1	<1	<1
COD	mg L ⁻¹	15	15	15
Ammonia	mg L ⁻¹ NH ₃ -N	0.0	0.0	0.0
Manganese	mg L ⁻¹	0.08	0.09	0.07

Source: Pathumthani Water Authority, Thailand (during August 2004 to May, 2005).

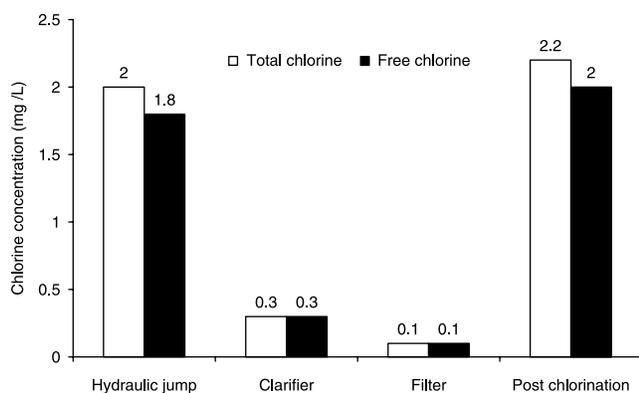


Figure 2 | Pre-and post total chlorine and free chlorine levels at Bangkhen water treatment plant (Hydraulic jump is used to mix the coagulants with the raw water that enters the clarifiers).

30 km away from the water treatment plant in Ladkrabang province, was selected. The transmission line consisted of pipes with 3,200 mm diameter for 5 km, 3,000 mm for 8 km and 2,000 mm for the rest 17 km. The total travel time from the water treatment plant to the reservoir was about 7.5 hours.

The Ladkrabang reservoir serves water via three trunk mains. In this research, the transmission line of 1,000 mm diameter, laid along the Ladkrabang road was selected. The length of the trunk main was about 9.0 km and the amount of water served via this line was approximately about 73,000 m³/d. The results obtained in this study are presented in Table 3. The data were obtained during the period of peak demand and this may cause smaller retention time of water in the distribution system. The residual chlorine in the samples was quenched properly by adding

NaHSO₅ at site immediately after measuring the chlorine concentration. These samples were brought back to the laboratory for THM analysis. The free chlorine concentration in the pipe line was greater than 0.2 mg L⁻¹ within the initial segment of 6 km from the reservoir. The residual chlorine concentration of 0.2 mg L⁻¹ at customers tap would supply disinfected water to the customers as microbial re-growth is suppressed at this concentration. The concentration required to disinfect different microorganisms in the treated water can be obtained using $C^n t$ values, where C denotes the concentration of the disinfectant, t denotes the contact time required to achieve the desired percentage of kill and n is a constant which is characteristic of a particular disinfectant (Berg 1964). The rest of the 3 km of the transmission line and all distribution networks connected to this segment of the line did not have enough residual effect to safeguard consumers. Therefore, it can be concluded that a booster chlorination system has to be introduced at the point where the residual chlorine level becomes lower than 0.2 mg L⁻¹. The introduction of booster chlorination can be optimised, providing a suitable dosage of chlorine at the reservoir.

The THM concentration within the whole transmission line was well below the WHO standards (CHCl₃ = 200 µg/L, CHCl₂Br = 60 µg/L, CHClBr₂ = 100 µg/L and CHBr₃ = 100 µg/L). Moreover, the level of THM did not vary and stayed as almost constant throughout the pipe line. But, the THM level could increase during the low flow conditions in the dry season, since the water treatment plant experiences comparatively high TOC in raw water, during those periods.

Table 3 | Free/Total Cl variation and TTHM formation along the distribution line (1000 mm in diameter) from Ladkrabang reservoir

Distance from Ladkrabang reservoir (km)	Time (h)	Free Cl (mg L ⁻¹)	Total Cl (mg L ⁻¹)	THM (µg L ⁻¹)				TTHM (µg L ⁻¹)
				CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃	
0.0 (At reservoir)	7.5	0.93	0.94	14.81	6.68	1.30	0.00	22.79
1.2	7.8	0.71	0.94	14.18	7.76	1.43	0.00	23.38
2.4	8.1	0.74	0.90	16.24	7.70	1.52	0.00	25.46
3.6	8.4	0.79	0.91	12.47	5.02	1.01	0.00	18.50
6.0	9.1	0.22	0.34	14.63	5.79	1.14	0.00	21.55
9.0	9.8	0.15	0.22	15.72	6.52	1.27	0.00	23.51

The time was measured from the Bangkhen water treatment plant.

Chlorine decay and THM formation under laboratory conditions

Water collected from Bangkokhen water treatment plant, just after filtration, was sent through the three resin columns arranged sequentially as DAX-8, XAD-4 and IRA-958. Figure 3(a) through 3(d) shows the model fitting of laboratory data obtained for total and free chlorine decay in treated water, DAX-8, XAD-4 and IRA-958 effluents, respectively. Parameter estimation was carried out to estimate the reaction rate constants k_1 through k_5 , initial concentrations (in mgL^{-1} of chlorine equivalents) of FRA, SRA, FRN and SRN using the free and total chlorine decay data obtained for treated water. Those reaction rates coefficients were kept constant and the initial values of

FRA, SRA, FRN and SRN were estimated for DAX-8, XAD-4 and IRA-958 effluents (using the free and total chlorine decay data obtained for those effluents). Thus, the sum of the initial concentrations of FRA, SRA, FRN and SRN will give the total chlorine demand of each water tested. Then the THM formation coefficients α and β were estimated for those waters using the THM data obtained from the experiments (Figure 4 shows the values of all these parameters for different effluents and shows the chlorine demand and THM formation potential of VHA, SHA, CHA and NEU).

From Figure 4, it can be seen that continuous removal of TOC through each resin. The contribution of VHA and SHA towards TOC is minimal (0.14 and 0.03 mgL^{-1} , respectively). However the contribution of CHA towards TOC is the largest (2.52 mgL^{-1}) and the contribution

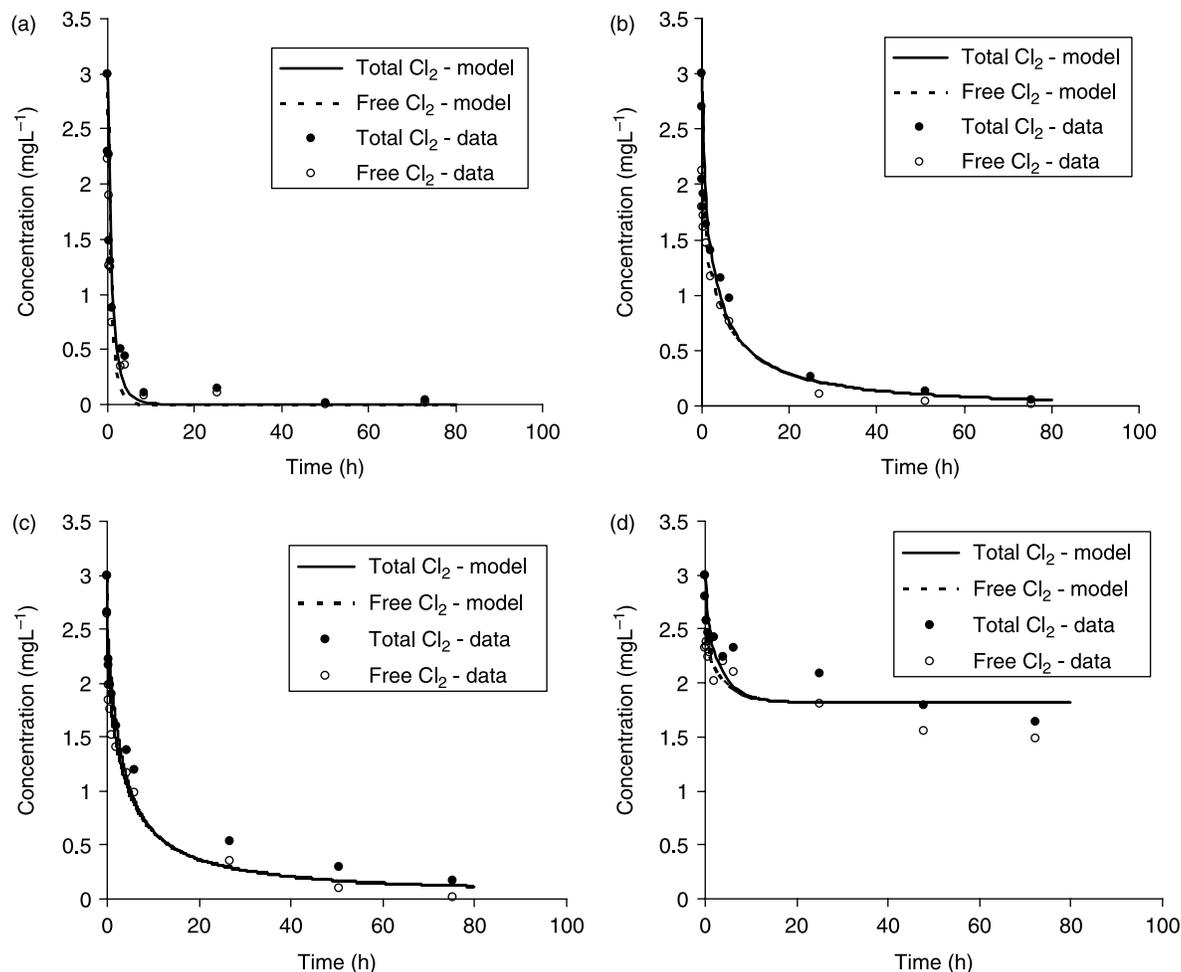
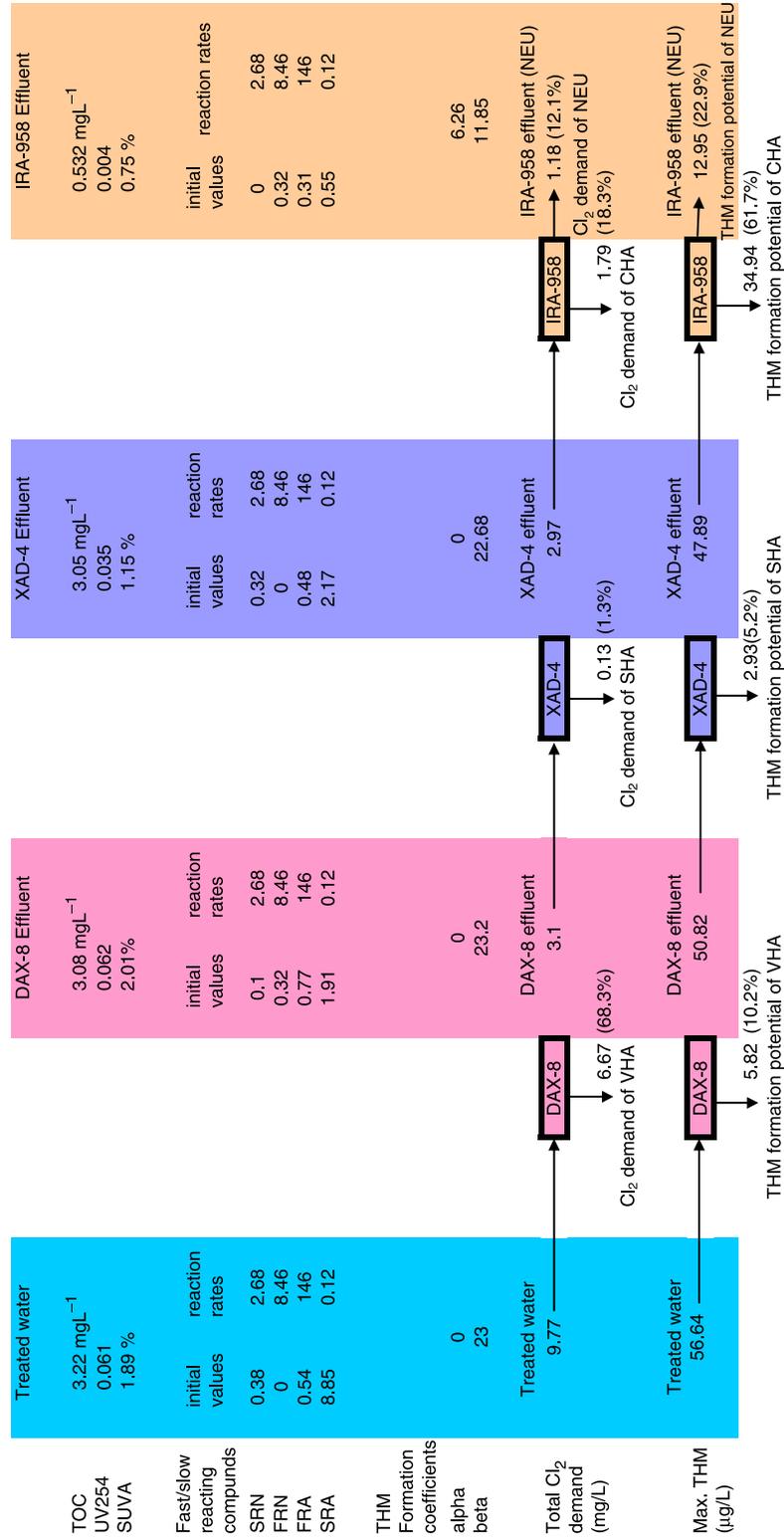


Figure 3 | Model fitting of free and total chlorine for water from Bangkokhen treatment plant. (a) Treated water. (b) DAX-8 effluent. (c) XAD-4 effluent. (d) IRA-958 effluent.



Initial values are in mgL⁻¹ chlorine equivalent; reaction rates are in Lmg⁻¹h⁻¹

Figure 4 | Chlorine demand and THM formation potential of different organic fractions in the Bangkok treated water.

of NEU is the second largest (0.53 mg L^{-1}). The SUVA values indicate that NEU comprised smaller organic molecules compared to those of CHA and SHA. VHA might have the smallest organic molecules as there is no change in absorption due to the removal of VHA by DAX-8 resin. However, for the Bangkhen water (total chlorine demand = 9.77 mg L^{-1}), VHA component has the highest chlorine demand mainly contributed by slow reacting agents (SRA). The chlorine demand decreases in the following order: VHA (68.3%), CHA (18.3%), NEU (12.1%) and SHA (1.3%). The slow reacting agents contribute to chlorine demand significantly in all types of waters and removing VHA from the Bangkhen treated water would reduce the chlorine demand significantly.

Figure 5 shows the model fitting of laboratory data obtained for THM in treated water, DAX-8, XAD-4 and IRA-958 effluents, respectively. The figure shows clearly that a significant reduction in THM formation when the CHA fraction is removed from the treated water through IRA-958 resin. The maximum THM formation in the treated water is $56.64 \mu\text{g L}^{-1}$ and the THM formation due to CHA is the largest at 61.7%. The THM formation of the other fractions are as follows: NEU (22.9%), VHA (10.2%) and SHA (5.2%). This clear indication shows that removing CHA from the water would reduce the TTHM formation in the system significantly. Further, α and β represent the THM formation coefficients which are due to the contribution of fast and slow reacting organic compounds to form THM, respectively.

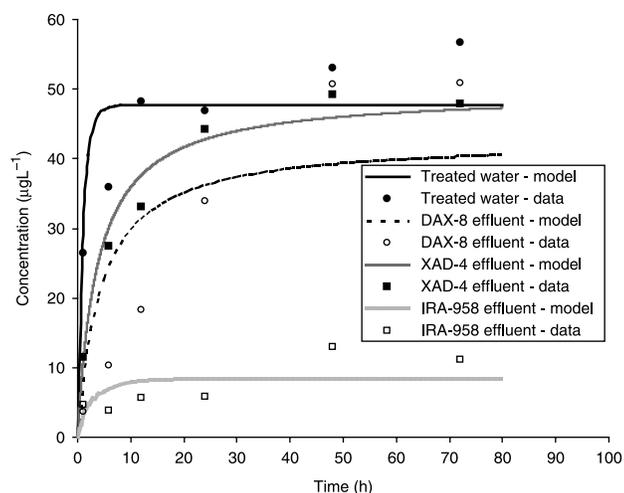


Figure 5 | Model fitting of TTHM data in Bangkhen water.

The value of α is small due to the absence of fast reacting organic compounds in treated water which has been pre-chlorinated. Thus, the THM formation is mainly due to the slow reacting agents.

When Chow *et al.* (2004) used a wide alum dose range ($30\text{--}180 \text{ mg L}^{-1}$ alum) to coagulate the water, the results showed the following: (i) the NEU fraction was hardly removed by alum treatment, (ii) The CHA fraction was readily removed in the underdosing and extreme overdosing conditions and (iii) both the SHA fraction and the VHA fraction were preferably removed in the alum dose range covering the conventional to enhanced coagulation. This indicates that process modification is required in a conventional water treatment plant to remove CHA fraction, if it contributes to significant THM formation.

The above study shows that, the Bangkhen water distribution system has to be modified with booster chlorination points. Further, the model output could be used in finding the elements which are contributing to the consumption of chlorine at the treatment plant other than the water itself; this allows better control of chlorine dosing at the treatment plant, which in turn will reduce the formation of DBPs. Further the model will accurately predict the decay due to the organic/inorganic and nitrogenous compounds that are remaining in the water at any point in the distribution system, which will indicate the status of the distribution system with respect to its chlorine consumption. Further, if re-chlorination is introduced in the distribution system downstream of the treatment plant the model will predict the chlorine decay due to the slow reacting organic and nitrogenous compounds accurately. Although the analyses in this study have been conducted for the water from Bangkhen treatment plant, seasonal variations were not considered. This must be carried out and the data obtained can be analysed using the model described in this study. This exercise is essential to understand the performance of the treatment plant throughout the year.

CONCLUSIONS

Several important factors on chlorine decay and THM formation in the Bangkhen water distribution system have

been found from this study. These findings can be used as common guidelines in designing water distribution systems which are similar to the system considered in this study.

- Initial concentration of FRA, SRA, FRN and SRN fractions in treated water: Rapid organic characterization technique can be used to evaluate the organic composition in treated waters. Chlorine decay and THM formation studies on the effluents emerging from the resins would help to find the organic fractions which are contributing significantly to chlorine demand as well to THM formation. This would then help to develop processes which could remove specific TOC that are in the raw water received by the water treatment plants.
- Reaction rates of organic constituents with free chlorine: chlorine decay tests have to be carried out to find the reaction rates. This will provide the immediate and total chlorine demand of the treated water. This would help to optimise the dosing of chlorine to have adequate residual effect throughout the distribution system.
- Length of the distribution system: the higher the length of a distribution system, the higher the potential for THM formation; thus, longer lines have to be checked for both excess THM and inadequate residual effect. THM formation model would help to determine the maximum THM formation in a distribution system.
- Total residence time of the system: The potential for THM formation can be increased by increased residence time. Therefore, the capacity of reservoirs and velocity of water have to be optimised to minimize the THM formation potential.
- Chlorine decay and THM formation models similar to the ones developed for Bangkok water treatment plant can be used to identify the exact locations to provide booster chlorination facilities.

ACKNOWLEDGEMENTS

The first author wishes to thank Mr. George Kastl and Dr. Ian Fisher of Sydney Water Corporation and CRC for Water Quality and Treatment for their inputs in the past in modelling the kinetics of chlorine decay.

REFERENCES

- Berg, G. 1964 The virus hazard in water supplies. *J. New Engl. Water Works Assoc.* **78**, 79.
- Biswas, P., Lu, C. & Clark, R. M. 1993 A model for chlorine concentration decay in pipes. *Water Res.* **27**(12), 1715–1724.
- Boccelli, D. L., Tryby, M. E., Uber, J. G. & Summers, R. S. 2003 A reactive species model for chlorine decay and THM formation under re-chlorination conditions. *Water Res.* **37**(11), 2654–2666.
- Bolto, B., Braun, G. B., Dixon, D., Eldrige, R., Frimmel, F., Hesse, S., King, S. & Toifl, M. 1999 Experimental evaluation of cationic polyelectrolyte for removing natural organic matter from water. *Water Sci. Technol.* **40**(9), 71–80.
- Chow, C. W. K., Fabris, R. & Drikas, M. 2004 A rapid fractionation technique to characterise natural organic matter for the optimization of water treatment process. *J. WSRT-Aqua* **53**(2), 85–92.
- Clark, M. R. 1998 Chlorine demand and TTHM formation kinetics: a second order model. *J. Environ. Eng.* **124**(1), 16–24.
- Frateur, I., Desloius, C., Kiene, L., Levi, Y. & Tribollet, B. 1999 Free chlorine consumption induced by cast iron corrosion in drinking water distribution systems. *Water Res.* **33**(8), 1781–1790.
- Hua, F., West, J. R., Barker, R. A. & Forster, C. F. 1999 Modelling of chlorine decay in municipal water supplies. *Water Res.* **33**(12), 2735–2746.
- Jegatheesan, V., Kim, S. H. & Joo, C. K. 2006 Evaluating the drinking water quality through an efficient chlorine decay model. *Water Sci. Technol. Water Supply* **6**(4), 1–7.
- Kastl, G. J., Fisher, I. H. & Jegatheesan, V. 1999 Evaluation of chlorine decay kinetics expressions for drinking water distribution system modelling. *J. WSRT-Aqua* **48**(6), 219–226.
- Kastl, G. J., Fisher, I. H., Jegatheesan, V., Chandy, J. & Clarkson, K. 2003 Prediction of chlorine and trihalomethanes concentration profile in bulk drinking water distribution systems from laboratory data. *Water Sci. Technol.* **3**(1–2), 239–246.
- Kiene, L., Lu, W. & Levi, Y. 1998 Relative importance of the phenomena responsible for chlorine decay in drinking water distribution systems. *Water Sci. Technol.* **38**(6), 219–227.
- Ozdemir, O. N. & Ger, A. M. 1998 Realistic numerical simulation of chlorine decay in pipes. *Water Res.* **32**(11), 3307–3312.
- Powell, J. C., Hallam, N. B., West, J. R., Forster, C. F. & Simms, J. 2000 Factors which control bulk chlorine decay rates. *Water Res.* **34**(1), 117–126.
- Reichert, P. 1994 AQUASIM - A tool for simulation and data analysis of aquatic systems. *Water Sci. Technol.* **30**(2), 21–30.

- Shafy, M. A. & Grunwald, A. 2000 **THM formation in water supply in South Bohemia, Czech Republic**. *Water Res.* **34**(13), 3453–3459.
- Snoeyink, V. L. & Jenkins, S. 1980 *Water Chemistry*. John Wiley & Sons, New York, USA.
- Sohn, J., Amy, G., Cho, J., Lee, Y. & Yoon, Y. 2004 **Disinfectant decay and disinfection by-products formation model development: chlorination and ozonation by-products**. *Water Res.* **38**(10), 2461–2478.
- Standard Methods for the Examination of Water and Wastewater* 1995 19th edition, APHA, AWWA, and WEF, Washington, USA.
- Vikesland, P. J., Ozekni, K. & Valentine, R. L. 2001 **Monochloramine decay in model and distribution system waters**. *Water Res.* **35**(7), 1766–1776.
- Wanner, O. & Reichert, P. 1996 **Mathematical modelling of mixed-culture biofilms**. *Biotechnol. Bioeng.* **49**, 172–184.

First received 28 June 2007; accepted in revised form 12 October 2007