Quantitative assessment of trihalomethane formation using simulations of reaction kinetics

Spyros K. Golfinopoulos[a,*], George B. Arhonditsis[b,1]

[a] *Department of Environmental Studies, University of the Aegean, Karadoni 17, 81100 Mytilene, Greece*
[b] *Department of Marine Sciences, University of the Aegean, 81100 Mytilene, Greece*

Abstract

A modelling procedure with a time discretisation of 1 min is developed in order to study and simulate the kinetics of formation of total trihalomethanes (TTHM) in water treatment plants. This methodology was applied on two significant processing units of Athens (Galatsi Treatment Plant-GTP, Menidi Treatment Plant-MTP). The fundamental concept of the model was based on the representation of the water treatment plant as a mixed flow reactor, where the formation of TTHM was predicated on a generalised reaction of total halogens with an organic precursor. Differential rates of reactants and products were expressed in terms of the reaction stoichiometry. Volatilisation, flocculation, coagulation and sedimentation processes were also incorporated in the model in order to assess their distinct role. The most appropriate coefficient set was sought and it was found that a stoichiometric ratio of 0.5 for total halogen, 0.6 for organic substrate and 0.2 for TTHM (or 2.5:3:1) resulted in the best fit between simulated and experimental data. The present modelling approach should be considered as a promising methodological basis towards the realistic reproduction of the dynamics of water treatment plants and the development of reliable numerical tools for the accurate prediction of THM formation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Trihalomethanes; Drinking water; Chlorination; Reaction kinetics; Quality modelling

1. Introduction

The presence of trihalomethanes (THM) in nation's drinking waters is of concern from health-related aspect, since these compounds have been related to cancer and reproductive outcomes [1–3]. Epidemiological studies have suggested a possible link between chlorination and chlorination by-products with excess risk of bladder and rectal cancer [3,4]. Therefore, new restrictive rules of surface water and maximum level of total THM (TTHM) in distribution systems are being imposed by the Safe Drinking Water Act and its Amendments (SDWAA). The European Union (EU) drinking water quality standard for TTHM is 100 µg/l [5]. Greece has no official guidelines or regulations for TTHMs [6,7] and applies the EU standard.

Because of the promulgated THM standard, it was considered advantageous to develop methodologies for predicting THM concentration as a function of time under various reaction conditions. THM evolution has been shown to be a function of many water quality parameters, including the total organic carbon (TOC), type of organic precursors, pH of chlorination, temperature, UV light absorbance, bromide level, and reaction time [8]. Various researchers have qualitatively and semi-quantitatively evaluated the effects of these factors on THM formation [9]. However, there is still a remarkable gap in existing literature concerning kinetics and reaction mechanisms, whereas the respective modelling constructions are oversimplified approaches that exclude important aspects of the issue.

*Corresponding author. Tel.: +30-251-36000; fax: +30-251-36099.

E-mail address: sgolf@env.aegean.gr (S.K. Golfinopoulos).

[1] Present address: Department of Civil and Environmental Engineering, University of Washington, 313B More Hall, Box 352700, Seattle, WA, USA.

Most dynamic quality models use simple limited n-th order kinetic relations for THM formation. Several works proposed differential rate expressions portraying the rate of THM production as a function of chlorine residual, TOC or a yield parameter f, which represented the moles of THMs formed per mole of free chlorine consumed. The reaction order with respect to these variables was greater or equal to unity, but the simulated results exposed discrepancies with experimental data indicating that this sort of relationships seems unlikely and that more work has to be done [10–12]. More recent studies model the kinetics of the THM species under representative extreme conditions employing the site-specific quality trends with stoichiometric expressions based on an average representative bromine content factor of the source [13]. This development was further combined with dynamic water quality transport models, and despite of several deviations at distant locations from the source it represents a useful and robust methodology for water utilities attempting to verify the SDWAA regulations regarding the THM species [14].

In the present work, a new modelling approach is developed in order to study and simulate the kinetics of formation of TTHMs. The fundamental concept of the model is based on the representation of the water treatment plant as a mixed flow reactor, where the formation of TTHM is based on a generalised reaction of total halogens with an organic precursor. Volatilisation and sedimentation (including flocculation, coagulation and gravity sand filtration) processes are also incorporated in the model in order to assess their distinct role in processing units. The present modelling construction provides the basis towards the development of a reliable methodological tool that can potentially assist the utilities' operators in abiding with quality rules.

2. Methodology

2.1. Study areas

All data for this study were obtained from Menidi (MTP) and Galatsi (GTP) Treatment Plants of Athens, Greece. Lakes Mornos, Marathon and Iliki are the significant bodies of fresh water in Athens. The MTP with a design capacity of 380,000 m^3/d receives water mainly from Mornos and sometimes from Iliki lake. It consists of two separate units: the old (unit 1) and the new unit (unit 2) treating 250,000 and 130,000 m^3/d, respectively. On the other hand, the GTP has a design capacity of 360,000 m^3/d receiving water mainly from Marathon and Iliki lakes and quite recently from boreholes, because of the draughts and the subsequent low yield of the above water bodies [15]. Both the plants are of conventional design: major features include

coagulation, flocculation, sedimentation of gravity sand filtration. Figs. 1 and 2 show the basic structure, the location of sampling and chlorination points of MTP and GTP, respectively [7,15,16].

The experimental procedure corresponds to a sampling period of six years (1993–1998). Duplicate samples for THMs measurement were collected monthly from each sampling location in 40 ml glass bottles and were capped with PTFE-faced silica septum (Pierce 13075), including samples containing raw water. Sample bottles were carefully filled just to overflowing, without passing air bubbles through sample or trapping air bubbles in sealed bottle. The bottles were prepared by washing with soap and water, rinsing with tap water, ultrapure water (Millipore: Milli-Ro 5 plus and Milli Q plus 185), acetone (Mallinckrodt Chemical Works St. Louis) and placing in an oven at 150°C for 2 h. HCl (4 drops 6N/40 ml) was added to each raw water sample to prevent biodegradation and dehydrohalogenation, while sodium thiosulfate (3 mg/40 ml) was also added to each sampling bottle as a reducing agent [17]. After sampling, the bottles stored in the dark at temperatures between 0 and 4°C, were carried by air to Mytilene for analysis in the Water and Air Quality Laboratory (WAQL) at the Department of Environmental Studies of the University of the Aegean.

2.2. Analytical procedure

All samples were analysed according to the respective procedure described in Standard Methods [18] and reported in previous works [6,7]. Especially, liquid-liquid extraction (LLE) and Gas Chromatography (GC) were used to measure the concentration of THM in the water samples.

The bromide ion concentrations in the raw and finished water were determined with the Phenol Red Colorimetric Method and the detection limit was 0.1 mg/l [17]. The TOC of the samples was also determined using a TOC analyser (Dohrmann 190). Finally, typical data including water temperature, pH, chlorine dose and free residual chlorine were also collected from the plants.

2.3. Data set

The variables used in the present work were TTHM (μg/l), total halogen (mg/l) and TOC (mg/l) concentrations in raw and finished water. The TTHM concentrations were computed by summing the values of the chlorinated products, which are chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$) and bromoform ($CHBr_3$). It was observed that raw water of both the plants exposed insignificant THM values, which were omitted from the following modelling procedure. The total halogen concentrations in raw water were the sum of the chlorine
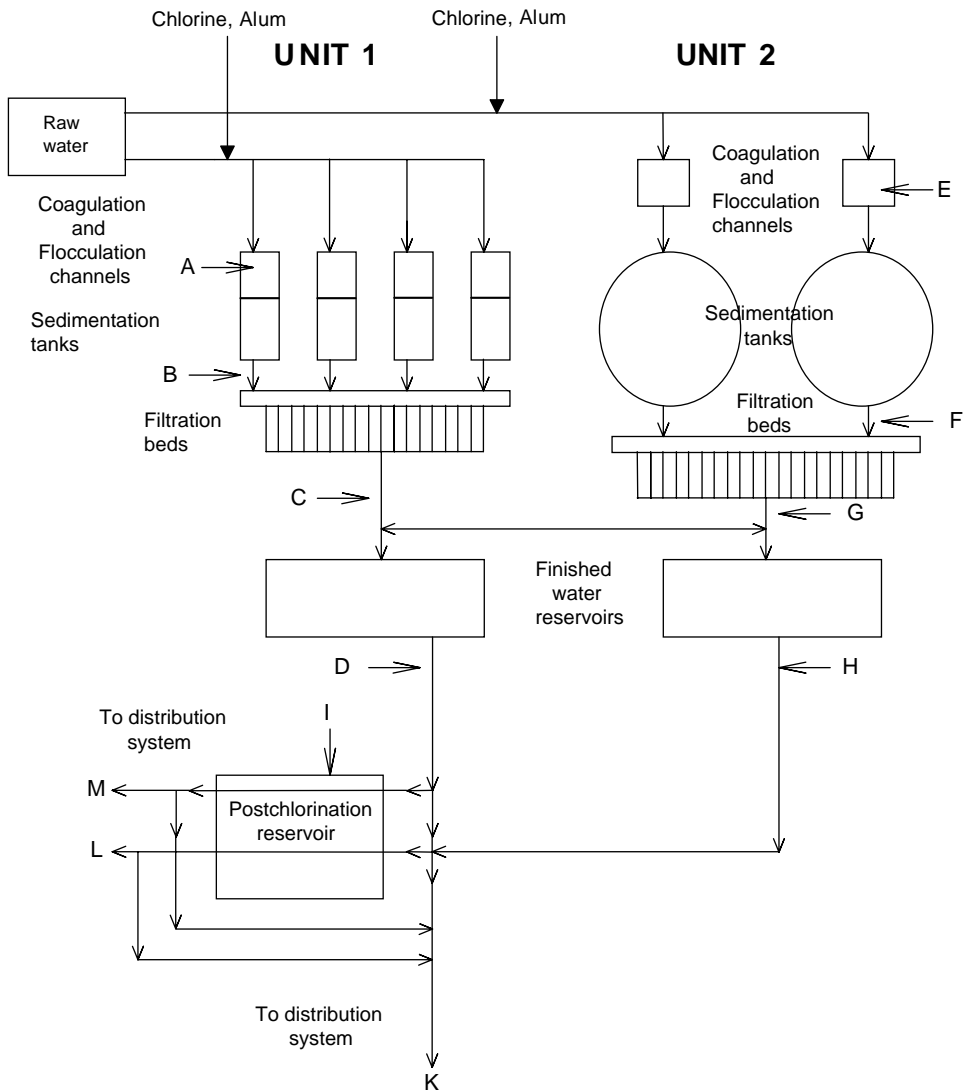
Fig. 1. Menidi treatment plant. (Sampling points given by the capitals A, B, C, D, E, F, G, H, I, K, L and M).

dose and the bromide ions, whereas the respective values in the finished water reservoir were associated with the free residual chlorine and also the bromide content. Moreover, the sum of pre- and postchlorination was used as chlorine dose, since the reaction is continued with the addition of chlorine during the latter step contributing to the further formation of THMs. The ranges of these variables, the means, the standard deviations and details concerning their spatial and temporal variability have been reported elsewhere [7,16].

Generally, the TTHM value measured in MTP (6–34 μg/l) were almost three times lower than those observed in GTP (15–82 μg/l), attributed mostly to the different quality of raw water. According to the data from the Department of Water Quality Control

(DWQC) of Athens Water and Sewage Corporation (AWSC) the concentrations of organic compounds in Iliki lake (the main supplier of GTP) are lying in high levels, while in Mornos lake (the main supplier of MTP) the organic content of water is lower. The main cause for this difference is the natural character of Iliki in contrast with Mornos, which is an artificial and well-protected lake from any source of contamination [7]. Another reason of the high THM concentrations in GTP is the high bromide level in the water of boreholes (0.31–1.30 mg/l), due to seawater intrusion to the groundwater and the possible contamination of the lake surface water from various anthropogenous and natural sources [15]. Thus, given the aforementioned differences in some essential water properties, the two plants provide a wide
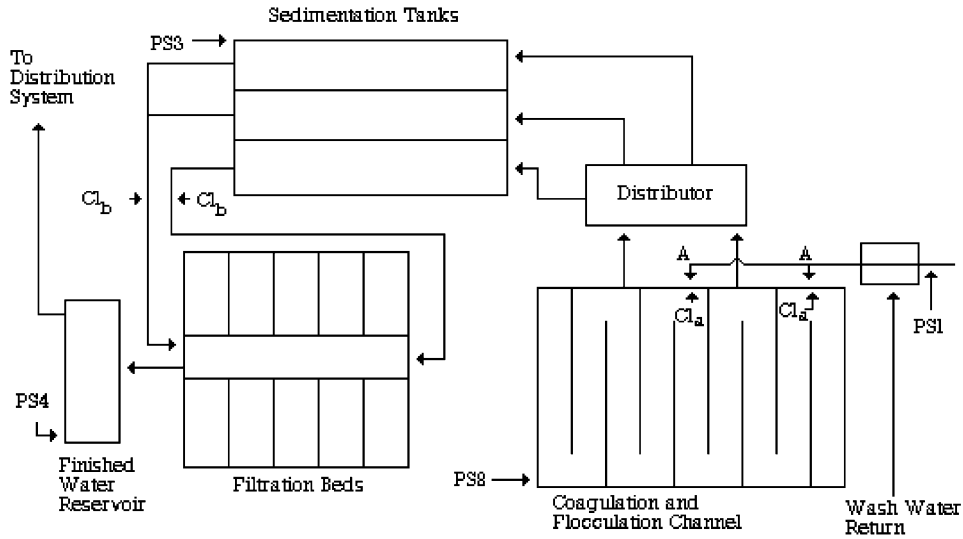
Fig. 2. Galatsi treatment plant. (PS: Points of Sampling, Cl_a: Point of prechlorination, Cl_b: Point of postchlorination).

range of conditions for testing the potential applicability of the present mathematical model.

2.4. The concept of the model

The fundamental concept of the present modelling procedure was based on the representation of the water treatment plant as a mixed flow reactor, illustrated schematically in Fig. 3, where the formation of TTHM is predicated on the following generalised reaction:

$$a_1[\text{Organic precursor}] + a_2[\text{Halogen}] \rightarrow a_3\text{TTHM}$$
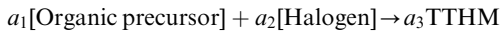
Hence, on the basis of the overall reaction stoichiometry, a differential rate expression was assumed relating the TTHM production to the a_2th power of the halogen and the a_1th power of the precursor concentration. The halogen term refers to the sum of the chlorine dose added for water disinfection and the bromide ion concentration in raw water, both constituting significant factors for the formation of halogenated by-products in finished drinking water. TOC was used as a surrogate parameter for the organic precursor, since it has resulted in the best fit among experimental and simulated data in previous modelling developments [9,19,20]. Moreover, according to the data from the DWQC of AWSC, the ammonia concentrations in the raw water of both the plants were very low (0.001–0.09 mg/l), and thus halogen (chlorine) consumption through conversion to stable monochloramine was considered negligible [21].

The principles of mass conversion in the completely mixed flow reactor have led into the following simple differential equations:
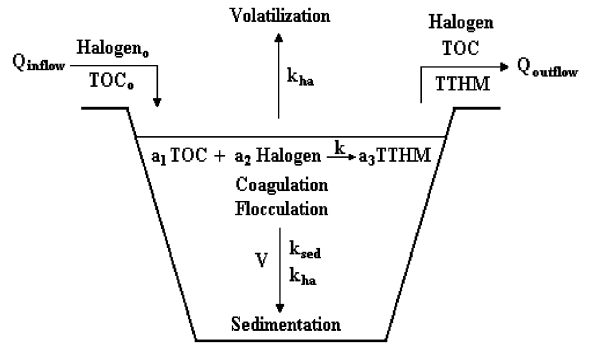

Fig. 3. The principle of the mixed flow reactor used for the representation of the water treatment plants.

$$\frac{V\, d[\text{TOC}]}{dt} = Q_{\text{inflow}}[\text{TOC}]_o - Q_{\text{outflow}}[\text{TOC}]$$
$$- kVa_1[\text{TOC}]^{a_1}[\text{Halogen}]^{a_2} - k_{\text{sed}}V[\text{TOC}],$$

$$\frac{V\, d[\text{Halogen}]}{dt}$$
$$= Q_{\text{inflow}}[\text{Halogen}]_o - Q_{\text{outflow}}[\text{Halogen}]$$
$$- kVa_2[\text{TOC}]^{a_1}[\text{Halogen}]^{a_2} - k_{\text{ha}}V[\text{Halogen}],$$

$$\frac{V\, d[\text{TTHM}]}{dt} = -Q_{\text{outflow}}[\text{TTHM}]$$
$$+ kVa_3[\text{TOC}]^{a_1}[\text{Halogen}]^{a_2},$$

where $[\text{TOC}]_o$ and $[\text{Halogen}]_o$ correspond to the raw water characteristics; whereas $[\text{TOC}]$, $[\text{Halogen}]$ and $[\text{TTHM}]$ are the respective values from the finished water reservoir in which the formation of TTHM is terminated [15]. The term $[\text{TTHM}]_o$ was neglected, since no THMs were detected in the raw water samples.

Furthermore, Q_{inflow} and $Q_{outflow}$ are the respective rates of raw water inflows and outflows in the finished water reservoir, both assumed to be equal and constant on a daily basis; V the volume of the tank (including all the stages of the water treatment plant except the finished water reservoir). The organic substrate losses due to flocculation, coagulation and sedimentation processes are denoted by the constant k_{sed}, whereas the exhaustion rate of the total halogens due to volatilisation and other potential paths in the plant is represented by the constant k_{ha}. Finally, the parameter k corresponds to the reaction constant, which is temperature-dependent, since the narrow range of the pH values in the specific data sets (Tables 1 and 2) disables the assessment of the effects of pH on reaction processes.

The set of differential equations defining the reaction processes in the compartments of the treatment plant was integrated with the fourth-order Runge-Kutta algorithm. Different integration time steps were tested and it was found that a time step of 1 min was sufficient to give accurate estimates of the reactants and the product in the 95% confidence interval. The calibration of the model was based on the "Controlled random search" method. The simulation was run for each sampling day separately and for a total simulation period equal to the retention time, which was presumed to coincide with the reaction time of chlorine and bromide ions with the organic substrate. Therefore, a basic assumption of the model was the maintenance of

the reaction during the residence time of a water mass in the system and the accomplishment of a steady-state behaviour just before it outflows in the finished water reservoir. The residence time for each sampling day was calculated by dividing the average water volume in the various stages of the plants (except the finished water reservoir) by the average flow rate for the specific day.

3. Results and discussion

The mean daily temperature, the pH and the respective values of the reaction constant (k), the sedimentation rate (k_{sed}) of the organic substrate and the exhaustion rate (k_{ha}) of the total halogens in GTP and MTP are reported in Tables 1 and 2, respectively. Meanwhile, it was found that in both cases, a stoichiometric ratio of 0.5 for total halogen, 0.6 for organic substrate and 0.2 for TTHM resulted in the best fit between simulated and experimental data, allowing a non-zero reaction rate that approaches steady-state conditions as the residence time expires. Both the plants are characterised by a mean retention time of 3.5 to 4.0 h [7]. The effects of the reaction stoichiometry and its implications with the model behaviour are discussed in the following paragraph. The variation of the reaction constant k was strongly dependent on the temperature; the maximum values (0.18–$0.19\,\mathrm{mg/l}^{-0.1} \times \mathrm{h}^{-1}$) were observed beyond the level of 20°C, whereas the lowest

Table 1
Mean daily temperature, pH and the respective values of the reaction constant (k), the sedimentation rate (k_{sed}) of the organic substrate and the exhaustion rate (k_{ha}) of the total halogens in the Galatsi treatment plant

Month	Temperature (°C)	pH	k ($\mathrm{mg/l}^{-0.1} \times \mathrm{h}^{-1}$)	k_{ha} (h^{-1})	k_{sed} (h^{-1})
September 94	22.75	7.42	0.18	0.38	0.62
August 94	21.63	7.38	0.16	0.39	0.63
October 94	21.00	7.51	0.16	0.38	0.62
July 93	20.25	7.39	0.15	0.41	0.61
June 93	19.75	7.35	0.15	0.42	0.62
July 94	19.75	7.39	0.15	0.36	0.64
October 93	19.50	7.48	0.15	0.33	0.66
June 94	18.75	7.42	0.15	0.33	0.65
September 93	18.50	7.56	0.14	0.38	0.71
August 93	18.25	7.47	0.13	0.35	0.70
November 93	16.75	7.52	0.12	0.26	0.65
November 94	16.28	7.66	0.14	0.24	0.60
May 93	15.00	7.70	0.11	0.24	0.70
May 94	14.00	7.42	0.09	0.22	0.58
April 93	13.50	7.35	0.11	0.22	0.58
December 94	12.38	7.68	0.05	0.23	0.65
December 93	12.33	7.53	0.07	0.19	0.65
April 94	12.33	7.48	0.05	0.18	0.65
January 95	11.00	7.39	0.04	0.21	0.65
January 94	10.68	7.52	0.07	0.19	0.65
February 94	10.00	7.44	0.05	0.20	0.65
March 94	10.00	7.48	0.07	0.22	0.65

Table 2
Mean daily temperature, pH and the respective values of the reaction constant (k), the sedimentation rate (k_{sed}) of the organic substrate and the exhaustion rate (k_{ha}) of the total halogens in the Menidi treatment plant

Month	Temperature (°C)	pH	k (mg/l$^{-0.1} \times$ h^{-1})	k_{ha} (h^{-1})	k_{sed} (h^{-1})
July 95	22.5	8.31	0.19	0.41	0.63
August 95	22.25	8.12	0.19	0.41	0.65
June 95	18.5	8.11	0.18	0.42	0.62
August 96	18.5	8.17	0.18	0.40	0.63
June 96	17.5	8.22	0.17	0.38	0.62
July 97	17.5	8.19	0.17	0.38	0.61
July 96	17.1	8.09	0.17	0.37	0.62
August 98	17	8.02	0.16	0.36	0.64
September 95	16.75	8.11	0.16	0.35	0.65
August 97	16.15	8.08	0.16	0.32	0.65
May 96	16	8.05	0.15	0.31	0.68
May 97	15.25	8.21	0.14	0.31	0.70
September 98	15	8.25	0.13	0.29	0.65
November 95	15	8.17	0.13	0.31	0.68
May 98	15	8.16	0.12	0.30	0.71
October 98	14.5	8.18	0.12	0.28	0.62
October 97	14.3	8.19	0.11	0.27	0.59
September 97	14.2	8.22	0.11	0.26	0.62
October 95	14	8.27	0.11	0.27	0.58
December 95	13.25	8.25	0.10	0.26	0.65
April 97	13.1	8.24	0.09	0.24	0.65
November 98	13	8.26	0.09	0.22	0.65
April 96	13	8.15	0.08	0.21	0.65
January 96	11.5	8.41	0.08	0.20	0.65
February 98	11	8.05	0.07	0.19	0.64
March 97	10	8.08	0.07	0.18	0.65
January 97	9.8	8.17	0.07	0.18	0.63
February 97	9	8.16	0.08	0.19	0.62
February 96	9	8.15	0.07	0.17	0.61
March 96	8.5	8.24	0.06	0.18	0.59
April 98	8.5	8.02	0.05	0.17	0.60
March 98	8	8.00	0.05	0.18	0.61

values (0.04–0.07 mg/l$^{-0.1} \times$ h^{-1}) occurred at temperatures below 10°C. Moreover, the discrepancies of the k values among the units at certain temperatures should be attributed to the different pH of the raw water, an effect that was not studied by the model. Similar trends characterised the exhaustion rate (k_{ha}) of the total halogens exposing its peaks (>0.38 h^{-1}) during the summer period, due to dechlorination from solar rays [22], while the winter values were lying in the level of 0.20 h^{-1}. The organic substrate losses (k_{sed}) due to flocculation, coagulation and sedimentation processes exhibited a temperature-independence, varying irregularly in the range of 0.60–0.70 h^{-1}.

It was observed that during the calibration procedure the various coefficient values and the respective stoichiometric ratios affected mostly the reaction rate. The effects of these ratios on the TTHM formation rate are represented in Fig. 4, where a kind of sensitivity analysis is performed after the calibration of the model for the

sampling of September 1994 in GTP. Thus, given the values of the rest constants are reported in Table 1, it can be seen that increasing values of the TTHM coefficient (a_3) lead to increasing reaction rates and after a value equal to 0.4 the system does not reach the steady-state within the residence time (Fig. 4a). Meanwhile, with a_3 values smaller than 0.2 the system exposes a zero reaction rate at brief time spans, shorter than the residence time. Fig. 4b shows the effects of the changes of the total halogens' coefficient (a_2), where it can be seen that values higher than 0.6 are associated with extreme initial TTHM formation rates (0.2–0.4 mg/1 h) accompanied by a rapid establishment of the steady-state conditions. Finally, the initial reaction rate seems to be independent from the TOC coefficient (a_1) values, but as the reaction time passes the lower the values the more rapid the decay of the formation rate (Fig. 4c). Similar inferences could be extracted from the rest sampling days, indicating the significance of the
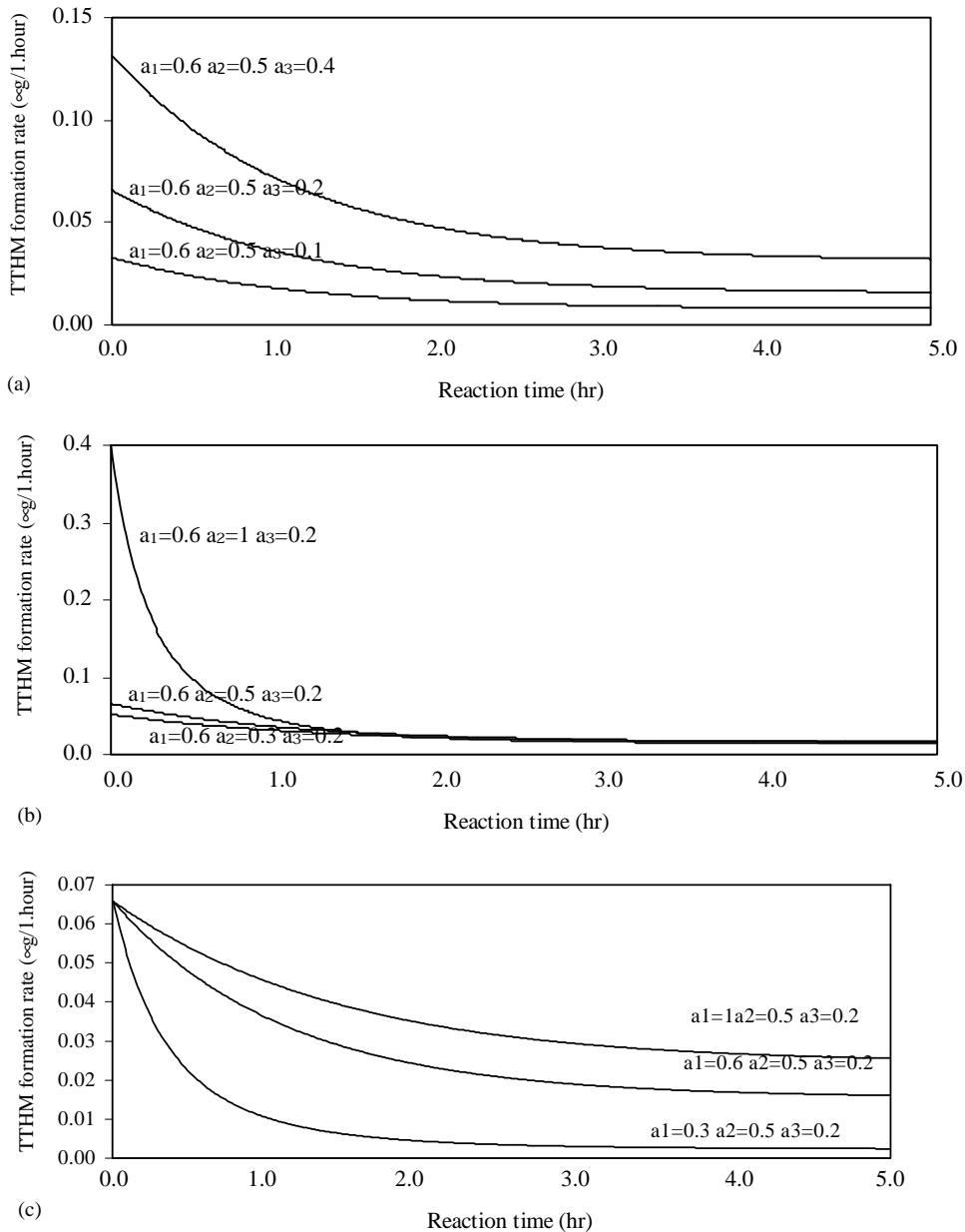
(a)

(b)

(c)

Fig. 4. Formation rates of total trihalomethanes for different stoichiometric ratios.

appropriate selection of reaction stoichiometry in the results. Conclusively, considering the model assumptions and the demand for (i) realistic reaction rates (rates that result in TTHM concentrations within the observed levels) and (ii) a reaction time that coincides with the residence time in the reservoir, the stoichiometric ratio 0.6:0.5:0.2 or (3:2.5:1) seems to give the optimum results, reproducing accurately the dynamics of water treatment plants.

The comparison between experimental and predicted values of TOC, total halogen and Trihalomethane concentrations in Galatsi and Menidi treatment plants is represented graphically in Figs. 5 and 6, respectively. It is observed that 78% (GTP) and 87% (MTP) of the predicted values fell within ±15% of the measured total halogen values. Similarly, TOC concentrations expose 82% (GTP) and 81% (MTP) agreement to within ±15% of the actual values, whereas the proportion of
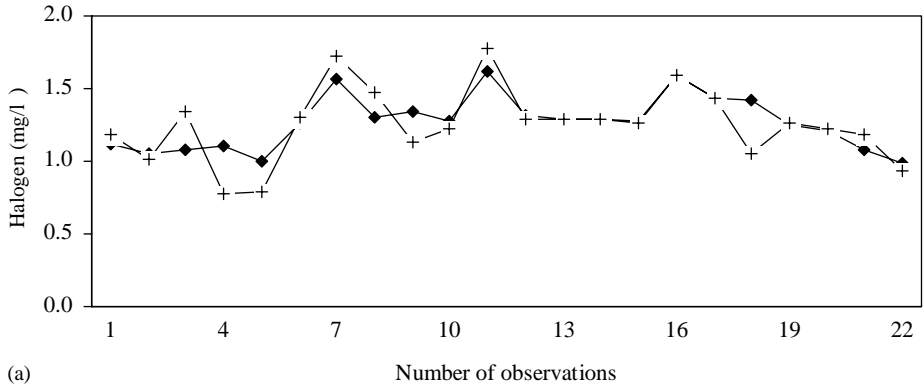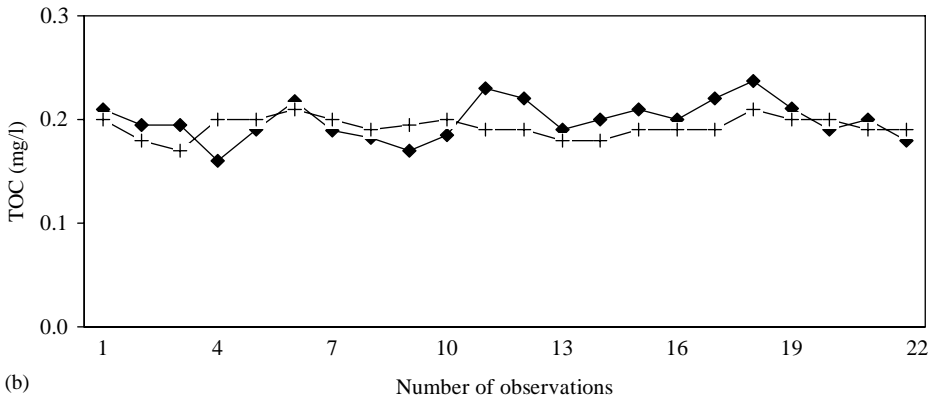
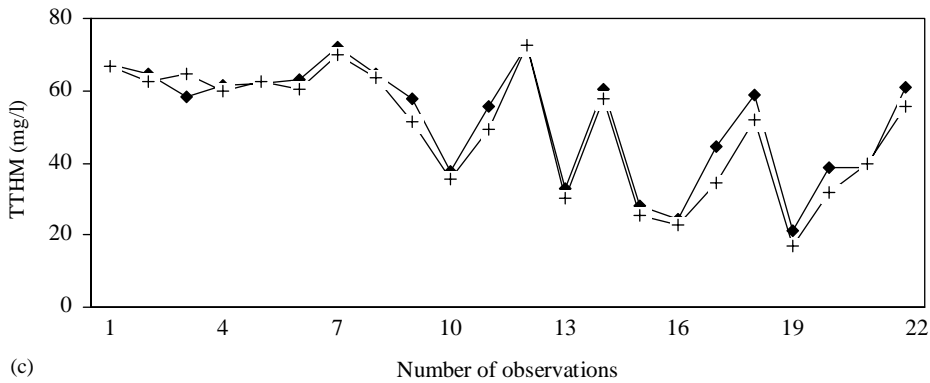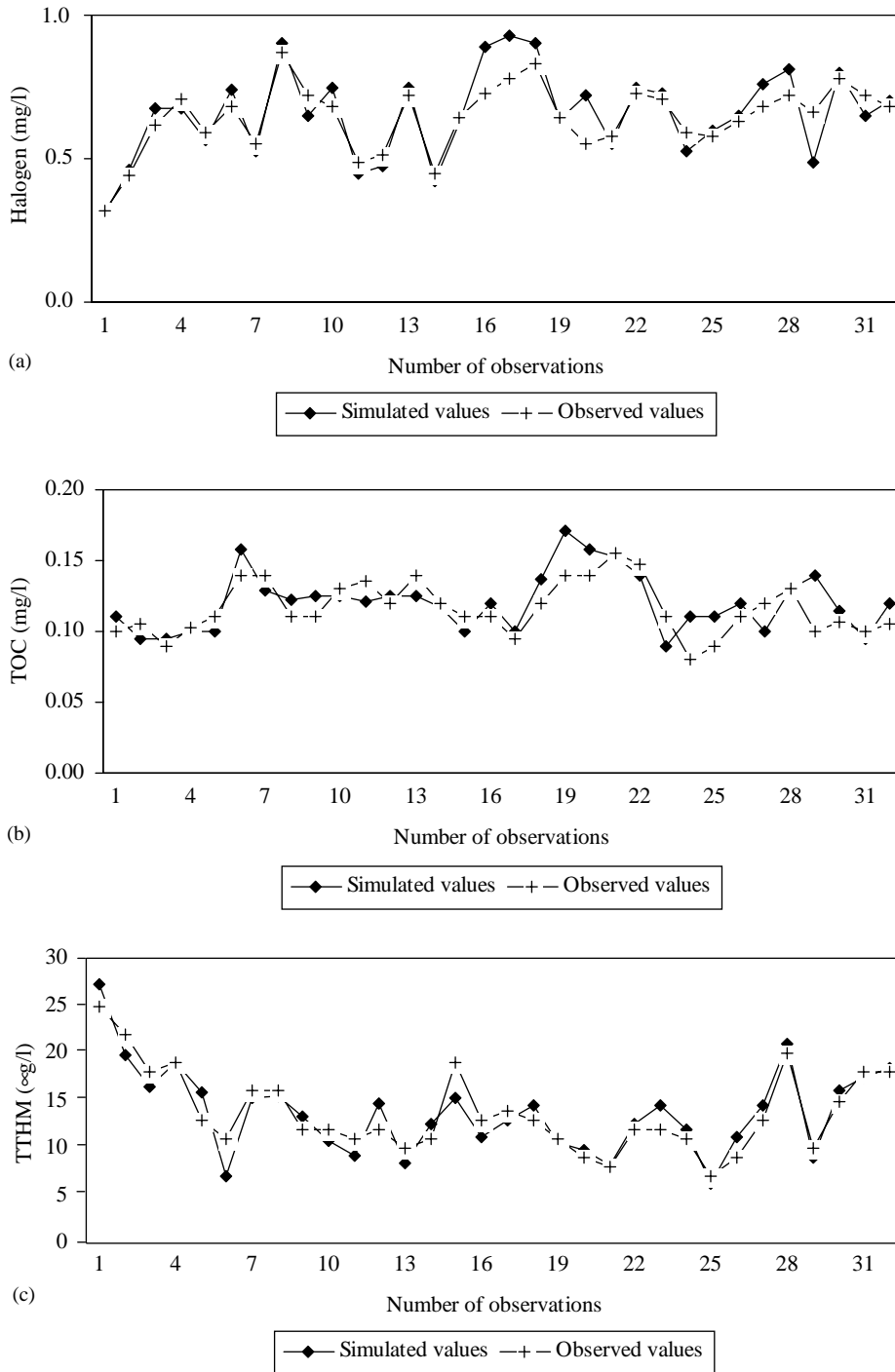Fig. 5. Diagram of predicted and measured values of (a) Halogen (b) TOC and (c) TTHM concentrations in the Galatsi treatment plant.

TTHM values lying in the same zone was 88% (GTP) and 79% (MTP), respectively. It can also be observed that this model accounts for a wide range of TTHM formation rates, including average values but also lows and highs over the annual cycle. The quantitative assessment of the goodness-of-fit between experimental and simulated TOC, total halogen and TTHM concentrations was performed by the two-sided
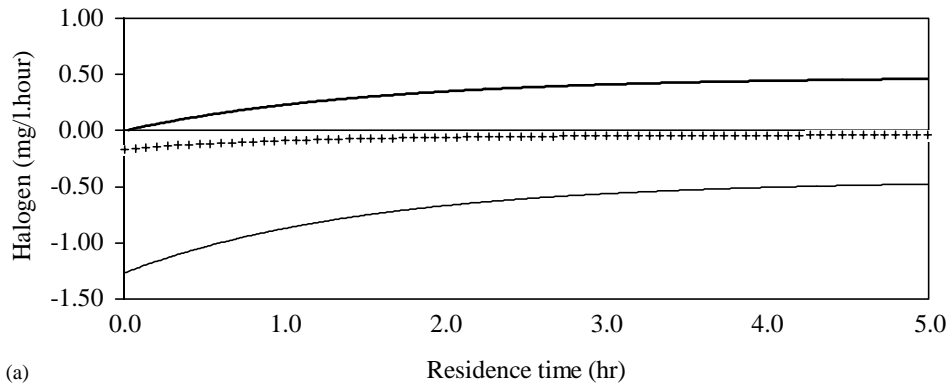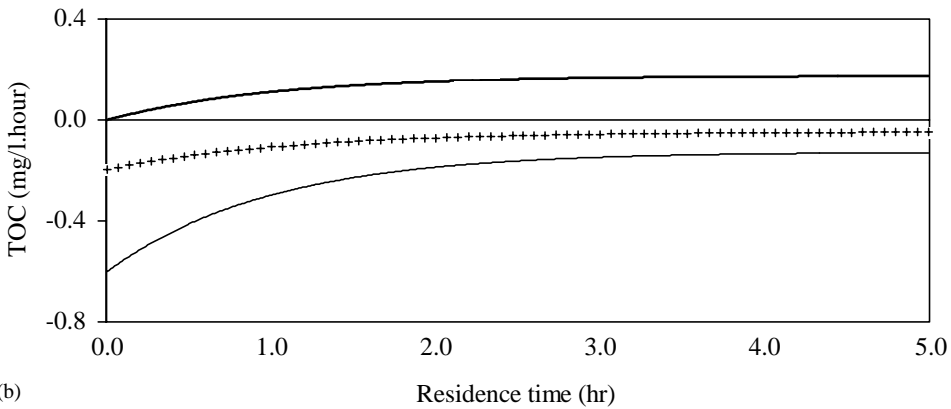
Fig. 6. Diagram of predicted and measured values of (a) Halogen (b) TOC and (c) TTHM concentrations in the Menidi treatment plant.

Kolmogorov-Smirnov test (Table 3). This statistical analysis is checking the maximum difference between simulated and observed distributions to determine if i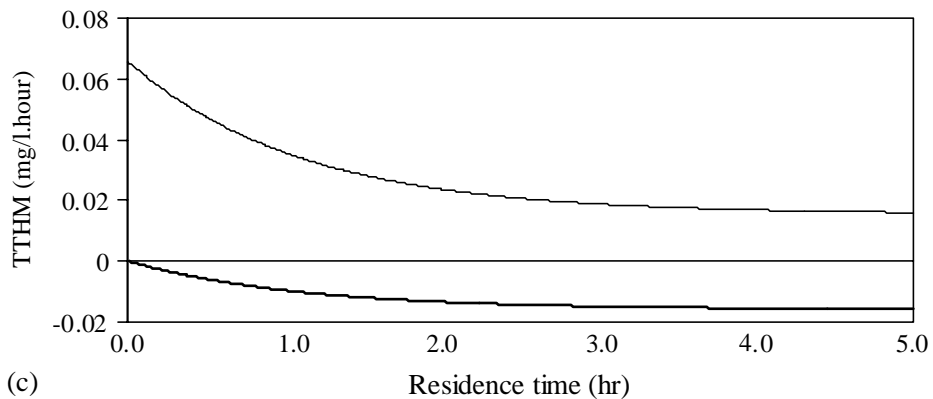t exceeds a critical value. Its nonparametric character has a much higher power than normal statistical techniques for analyses of data sets involving small sample sizes and skewed distributions, i.e. the experimental and computed data sets outflowing from these processing units

Fig. 7. Variability of the various sources and sinks of (a) Halogen (b) TOC and (c) TTHM, during the processing of water in a treatment plant. (Data obtained from the sampling of September 1994 in Galatsi treatment plant).
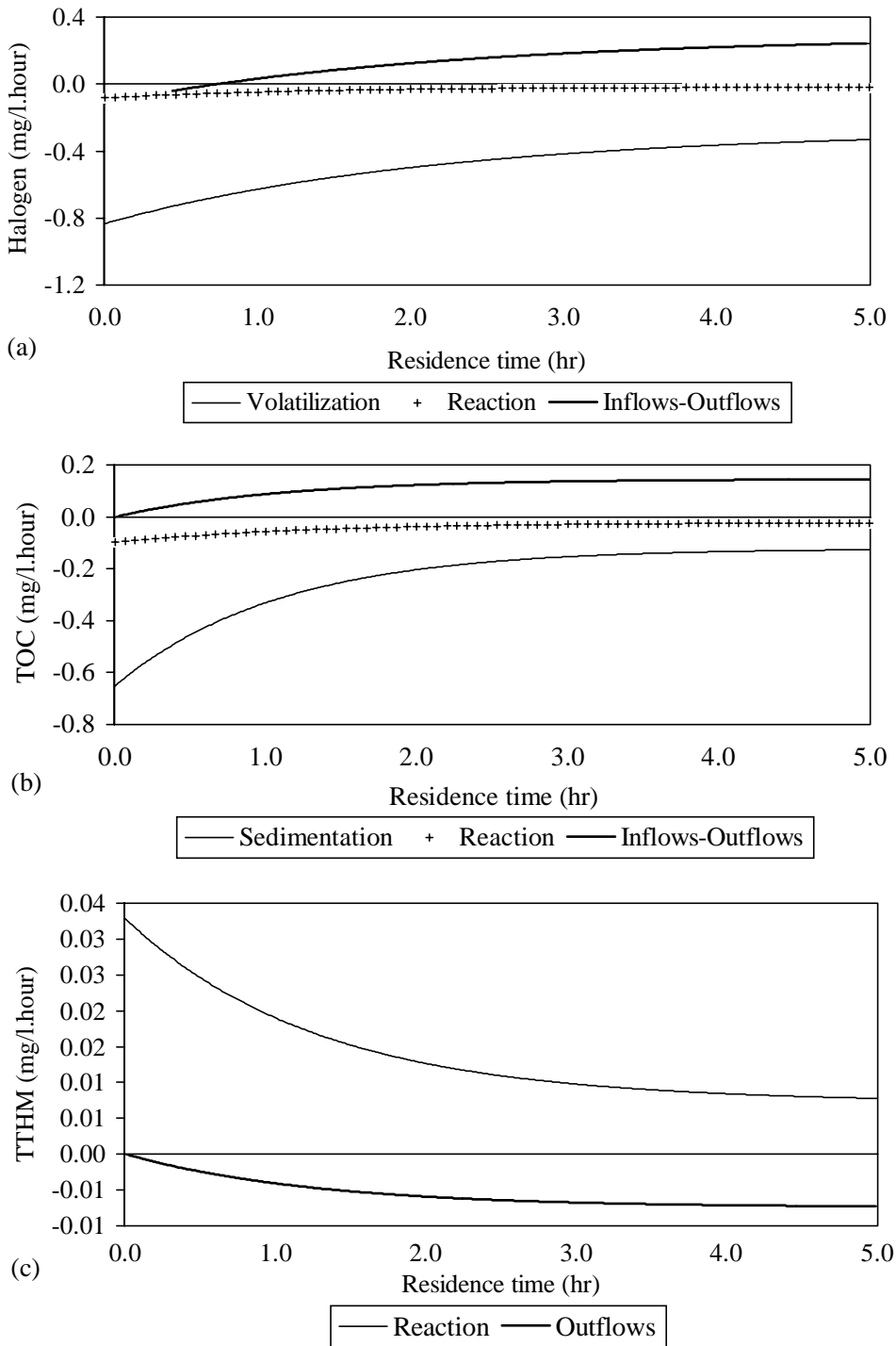
Fig. 8. Variability of the various sources and sinks of (a) Halogen (b) TOC and (c) TTHM, during the processing of water in a treatment plant. (Data obtained from the sampling of February 1994 in Galatsi treatment plant).

Table 3
Results of the two-sided Kolmogorov–Smirnov goodness-of-fit test between experimental and simulated values of TOC, halogen and trihalomethane concentrations

Variable	Galatsi water treatment plant		Menidi water treatment plant	
	K–S	K–S$_{0.05,22}$	K–S	K–S$_{0.05,32}$
TOC	0.154[a]	0.363	0.178[a]	0.312
Halogen	0.265[a]	0.363	0.242[a]	0.312
TTHM	0.205[a]	0.363	0.179[a]	0.312

[a] Good accordance between simulated and experimental data at the 0.05 level of significance.

[23]. Based on a 0.05 probability cut-off for the 95% confidence interval, the statistics in Table 3 indicate that the simulated values do not vary significantly from those monitored in both the plants. Therefore it can be inferred that this model development, based on the simulation of reaction kinetics in a mixed flow reactor, provides accurate estimates of the TOC, total halogen and TTHM concentrations.

The simulation model was further applied for assessing the contribution of various exogenous and endogenous sources and sinks of the reactants and the product in water treatment plants. The following results concern the sampling of September (Fig. 7) and February 1994 (Fig. 8) in GTP, in order to associate the magnitude of various processes rates with seasonality effects. The two sampling days were characterised by almost similar raw water characteristics (pH 7.4, total halogens 3.0 mg/l and TOC 1.2 mg/l), whereas the respective values of the constants are reported in Table 1. (The negative and the positive sign of the rates indicated in Figs. 7 and 8 correspond to sinks and sources, respectively). It can be seen that the initial volatilisation rate during September (1.2 mg/l h) was 33% greater than February (0.8 mg/l h) and as the residence time was passing accompanied by the establishment of steady-state conditions, a constant difference of 0.1 mg/l h was observed between the two months. Moreover, initial halogen and TOC sinks due to reaction rates exposed deviations in the level of 50% (0.2 and 0.1 mg/l h during September and February, respectively), also attributed to temperature effects. On the other hand, both the cases exposed a similar sedimentation rate (0.6 and 0.2 mg/l h) of the organic compounds, indicating the temperature-independence of this process in the plants. Finally, the initial TTHM formation rate of September (0.07 mg/l h) was almost double comparing with February's values (0.035 mg/l h), a difference that remained constant (0.02 and 0.01 mg/l h, respectively) until the end of the reaction time. Conclusively, the quantitative assessment of the roles of various processes and their association with various

factors (i.e. ambient conditions, raw water characteristics) is in good accordance with what is frequently reported in literature [12,24]; implying that the representation of water treatment plants as completely mixed flow reactors can give realistic approximations.

4. Conclusions

The present modelling approach has a good fit to the experimental data and describes sufficiently the kinetics of formation of TTHM in water treatment plants, based on a generalised reaction of total halogens with TOC. It has enabled the assessment and the clarification of the role of various processes, such as volatilisation of total halogens and sedimentation of organic substances in water treatment plants. Although relevant to reactants represented by aggregated entities, the model provides a reliable basis for additional modelling efforts with a view of identifying the reaction mechanisms under various compounds or conditions and developing effective estimators of THM concentrations. However, it is important to underline that both the stoichiometric ratio and the constants' values are strongly related to the concept of the representation of the processing units as a mixed flow reactor and the respective model assumptions. Thus, the potential generalisation of the present results and their association with real conditions seems to be rather dicey and should be verified by more complicated modelling developments.

The useful improvement of the present method could be the application of the model into the separate stages of the water treatment plants (coagulation and flocculation channels, sedimentation tanks or filtration beds) for quantifying the rates of various processes and partitioning their contribution into THM formation. Another trial should consider the role of the precursor type (i.e. humic or fulvic acids) and the composition of the organic matter, since it has been observed that different precursors result in varying yields and rates of THM formation [8]. Furthermore, the discrimination between the two fractions (i.e. chlorine dose and bromide ions) of the total halogen stock or even more between pre- and post-chlorination dose (significant differences on a kinetic basis), the separate modelling of several precursor-halogen type combinations are likely to provide the framework for studying the reaction kinetics of individual THM species and predict the respective concentrations. Finally, the present form of the model should be supported with more experimental data concerning both direct and interaction effects of raw water characteristics with ambient conditions on the constants' values; especially the constant k_{ha} of the exhaustion rate of total halogens and the reaction constant k that seemed to be dependent on solar radiation, pH and temperature values [25,12,22].

References

[1] Fayad NM. Seasonal variations of THMs in Saudi Arabian drinking water. J Am Water Works Assoc 1993;85(1):46–50.

[2] Nieuwenhuijsen MJ, Toledano MB, Eaton NE, Elliott P. Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. Occup Environ Med 2000;57:73–85.

[3] Simpson KL, Hayes KP. Drinking water disinfection by-products: an Australian perspective. Water Res 1998;32(5):1522–8.

[4] Craun GF, Epidemiological studies of organic micropollutants in drinking water. In: Hutzinger O, editor. Handbook of environmental chemistry. Water pollution, vol. 5. Berlin: Springer, Part A, 1991. p. 1–44.

[5] EECD (European Economic Community Directive). Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official J L 330, 05/12/1998, 1998. p. 32–54.

[6] Golfinopoulos SK, Kostopoulou MN, Lekkas TD. Volatile halogenated organics in the water supply system in Athens, Greece. Water Res 1998;32(6):1811–8.

[7] Golfinopoulos SK. The occurrence of trihalomethane in the drinking water in Greece. Chemisty 2000;41(11):1761–7.

[8] Amy GL, Chadic PA, Chowdhury ZK. Developing model for predicting trihalomethane formation kinetics. J Am Water Works Assoc 1987;79(7):89–97.

[9] Engerholm BA, Amy GL. A predictive model for chloroform formation from humic acid. J Am Water Works Assoc 1983;75(10):418–23.

[10] Clark RM. Chlorine demand and THM formation kinetics: a second-order model. J Environ Eng, ASCE 1998;124(1):16–24.

[11] Kavanaugh MC, Trussell AR, Cromer J, Trussell RR. An empirical kinetic model of THM formation: application to meet the proposed THM standards. J Am Water Works Assoc 1980;72(10):578–82.

[12] Trussell RR, Umphres MD. The formation of traihalomethanes. J Am Water Works Assoc 1978;70(11):604–12.

[13] Elshorbagy WE. Kinetics of THM species in finished drinking water. J Water Resources Plan Manage, ASCE 2000;126(1):121–8.

[14] Elshorbagy WE, Abu-Qdais H, Elsheamy K. Simulation of THM species in water distribution systems. Water Res 2000;34(13):3431–9.

[15] Golfinopoulos SK, Kostopoulou MN, Lekkas TD. THM formation in the high bromide water supply of Athens. J Environ Sci Health A 1996;31(1):67–81.

[16] Golfinopoulos SK, Xilourgidis NK, Kostopoulou MN, Lekkas TD. Use of a multiple regression model for predicting Trihalomethane formation. Water Res 1998;32(9):2821–9.

[17] APHA, Standard methods for the examination of water and wastewater, 17th ed. Washington, DC: American Public Health Association, 1989.

[18] APHA, Standard methods for the examination of water and wastewater, 18th ed. Washington, DC: American Public Health Association, 1992.

[19] Harrington GW, Chowdhury ZK, Owen DM. Developing a computer model to simulate DBP formation during water treatment. J Am Water Works Assoc 1992;84(11):78–87.

[20] Ivancev-Tumbas I, Dalmacija B, Tamas Z, Karlovic E. The effect of different drinking water treatment processes on the rate of chloroform formation in the reactions of natural organic matter with hypochlorite. Water Res 1999;33(18):3715–22.

[21] Johnson DJ, Jensen JN. THM and TOX formation: routes, rates and precursors. J Am Water Works Assoc 1986;78(4):156–62.

[22] Veenstra JN, Schnoor JL. Seasonal variation in trihalomethanes levels in an Iowa river water supply. J Am Water Works Assoc 1980;72(10):583–90.

[23] Hartigan JP, Quasebarth TF, Southerland E. Calibration of NPS model loading factors. J Environ Eng, ASCE 1983;109(6):1259–72.

[24] Sketchell J, Peterson HG, Christofi N. Disinfection by-product formation after biologically assisted GAC treatment of water supplies with different bromide and DOC content. Water Res 1995;29(9):2635–42.

[25] Nokes CJ, Fenton E, Randall CJ. Modelling the formation of brominated trihalomethanes in chlorinated drinking waters. Water Res 1999;33(17):3557–68.