

## Modeling the formation of chlorination by-products in river waters with different quality

Anastasia D. Nikolaou<sup>a,\*</sup>, Spyros K. Golfinopoulos<sup>a</sup>,  
George B. Arhonditsis<sup>b</sup>, Vassilis Kolovoyiannis<sup>c</sup>,  
Themistokles D. Lekkas<sup>a</sup>

<sup>a</sup> Department of Environmental Studies, University of the Aegean, Water and Air Quality Laboratory, University Hill, 81100 Mytilene, Greece

<sup>b</sup> Department of Civil and Environmental Engineering, University of Washington, 313B More Hall, Box 352700, Seattle, WA, USA

<sup>c</sup> Department of Marine Sciences, University of the Aegean, University Hill, 81100 Mytilene, Greece

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### Abstract

Water chlorination results in formation of a variety of organic compounds, known as chlorination by-products (CBPs), mainly trihalomethanes (THMs) and haloacetic acids (HAAs). Factors affecting their concentrations have been found to be organic matter content of water, pH, temperature, chlorine dose, contact time and bromide concentration, but the mechanisms of their formation are still under investigation. Within this scope, chlorination experiments have been conducted with river waters from Lesvos island, Greece, with different water quality regarding bromide concentration and organic matter content. The factors studied were pH, time and chlorine dose. The determination of CBPs was carried out by gas chromatography techniques. Statistical analysis of the results was focused on the development of multiple regression models for predicting the concentrations of total trihalomethanes and total HAAs based on the use of pH, reaction time and chlorine dose. The developed models, although providing satisfactory estimations of the concentrations of the CBPs, showed lower correlation coefficients than the multiple regression models developed for THMs only during previous study. It seems that the different water quality characteristics of the two river waters in the present study is responsible for this phenomenon. The results indicate that under these conditions the formation of THMs and HAAs in water has a more stochastic character, which is difficult to be described by the conventional regression techniques.

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### 1. Introduction

Chlorination of water results in the formation of a wide range of organic compounds, chlorination by-products (CBPs), which include trihalomethanes

(THMs) (Rook, 1974), haloacetic acids (HAAs) (Miller and Uden, 1983), haloacetonitriles, haloacetones and chloropicrin (Krasner et al., 1989; Nikolaou et al., 1999). These compounds have adverse health effects on human beings. Many of them have been classified as probable or possible human carcinogens and have been regulated by EPA (1996), WHO (1995) and the European Union (EEC, 1998). The maximum contaminant level (MCL) of 100 µg/l for the concentration of total THMs in

\* Corresponding author. Fax: +30-22510-36099.

E-mail address: [nnikol@aegean.gr](mailto:nnikol@aegean.gr) (A.D. Nikolaou).

drinking water set by USEPA in 1979 was later lowered to 80 µg/l. The sum of concentrations of five HAAs (monochloro-, dichloro-, trichloro-, monobromo- and dibromoacetic acid) has also been regulated by USEPA to 60 µg/l (Pontius, 1993; USEPA, 1998). The European Union guidelines for total THMs concentration in drinking water are 150 µg/l until 2008 and 100 µg/l after 2008 (EEC, 1998). The WHO guidelines are 200 µg/l for chloroform, 60 µg/l for dichlorobromomethane, 100 µg/l for dibromochloromethane, 90 µg/l for dichloroacetonitrile and 100 µg/l for dibromoacetonitrile (WHO, 1995).

The formation of CBPs has been found to depend on chlorine dose and residual, contact time, temperature, pH, natural organic matter and bromide concentration (Singer, 1994; Pourmoghaddas and Stevens, 1995; Nikolaou et al., 2000; Nikolaou and Lekkas, 2001).

The objectives of the present paper were the following:

- (a) To investigate the formation of CBPs, mainly THMs and HAAs, during chlorination of river waters with different quality regarding organic matter content (expressed as UV-272 absorbance) and bromide concentration. The effect of pH, contact time and chlorine dose was studied.
- (b) To develop predictive models for the concentrations of total THMs and total HAAs formed during chlorination of these river waters. Modeling of CBPs formation can be helpful to the minimization of their formation during water treatment, and therefore to compliance with the legislative measures and to protection of human health. Predictive models providing sufficient estimations of the concentrations of THMs and HAAs, the main CBPs occurring in chlorinated waters, could minimize the need of complicated and expensive analysis of these compounds in the finished waters.
- (c) To statistically evaluate the developed models (correlation coefficient, Durbin–Watson estimate), in comparison to the models developed during previous studies for THMs only (Golfinopoulos et al., 1998; Golfinopoulos and Arhonditsis, 2002a) using the same modeling technique (multiple regression), for both different water sources studied.

## 2. Materials and methods

### 2.1. Analytical procedure

Preparation of all glassware used during analysis included washing with detergent, 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.

Methanol purge and trap grade was purchased from Sigma-Aldrich, methyl-*tert*-butyl ether (MTBE) for organic trace analysis, potassium dichromate, potassium iodide, sodium sulfite, sodium sulfate anhydrous, copper (II) sulfate pentahydrate and sulfuric acid concentrated ISO for analysis from Merck and boric acid (zur Analyse) from Ferak. Ultrapure water was from Milli-Q water purification system (Millipore: Milli-Ro 5 plus and Milli Q plus 185). Stock solutions were prepared in MTBE by addition of monochloroacetonitrile (MCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), monobromoacetonitrile (MBAN), dibromoacetonitrile (DBAN), 1,1-dichloropropanone (1,1-DCP), 1,3-dichloropropanone (1,3-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), chloral hydrate (CH) and chloropicrin (CP) (Chemservice, purity > 99%). For THMs certified commercial mix solutions (Chemservice, purity > 99%) of known concentration were used. HAAs and their methyl esters as well as commercial mix solutions of HAAs and their methyl esters in MTBE were purchased from Supelco and were also accompanied with certificates of analysis (purity > 99%). The nine HAAs were monochloroacetic acid (MCA), monobromoacetic acid (MBA), dichloroacetic acid (DCA), bromochloroacetic acid (BCA), trichloroacetic acid (TCA), dibromoacetic acid (DBA), bromodichloroacetic acid (BDCA), dibromochloroacetic acid (DBCA) and tribromoacetic acid (TBA).

Water samples were collected in March 2000 from two rivers in Mytilene island, Greece. The rivers of Mytilene are small and the flow is not continuous throughout the year, due to the warm summer months. The river of Mytilene with the largest catchment area is Tsiknias river (catchment area 95 km<sup>2</sup>), followed by Mylopotamos river (catchment area 50 km<sup>2</sup>).

Samples were stored at 1-l amber glass vials and, kept at 4 °C, they were transported to the Water and Air Quality Laboratory of the University of Aegean. There pH measurements with use of a Crison MicroH2001 pH meter and sample filtration with Whatman GF/A glass microfibre filters 4.7 cm were performed. Samples were also analyzed for chloride, bromide and nitrate ions by a modification of EPA Method 300.0 (O' Dell et al., 1984). A Dionex 2000i ion chromatograph was used, with column Dionex HPLC-AG4A and suppressed conductivity detector. The analytical conditions were the following: Eluant NaHCO<sub>3</sub> 0.75 mM–Na<sub>2</sub>CO<sub>3</sub> 2.2 mM (flow 1.3 ml/min), regenerant H<sub>2</sub>SO<sub>4</sub> 25 mN (flow 3 ml/min).

Chlorination of the samples was performed according to the procedure described in Standard Methods for the Examination of Water and Wastewater (Iodometric Method I 4500B) (APHA, 1992). Prior to chlorination, pH was adjusted to the desired value (the pH values tested were 4, 5, 6, 7, 8, 9, 10 and 11) by addition of HCl or NaOH solution. The chlorinated samples (the chlo-

Table 1  
 Characteristics (pH, T, UV-272, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) of the river waters studied

	pH	T (°C)	UV-272 (cm <sup>-1</sup> )	Cl <sup>-</sup> (mg/l)	Br <sup>-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)
Tsiknias	7.07	14	0.048	15.5	nd <sup>a</sup>	5.5
Mylopotamos	7.70	14	0.262	143.9	2.5	4.5

<sup>a</sup> nd: not detectable concentration.

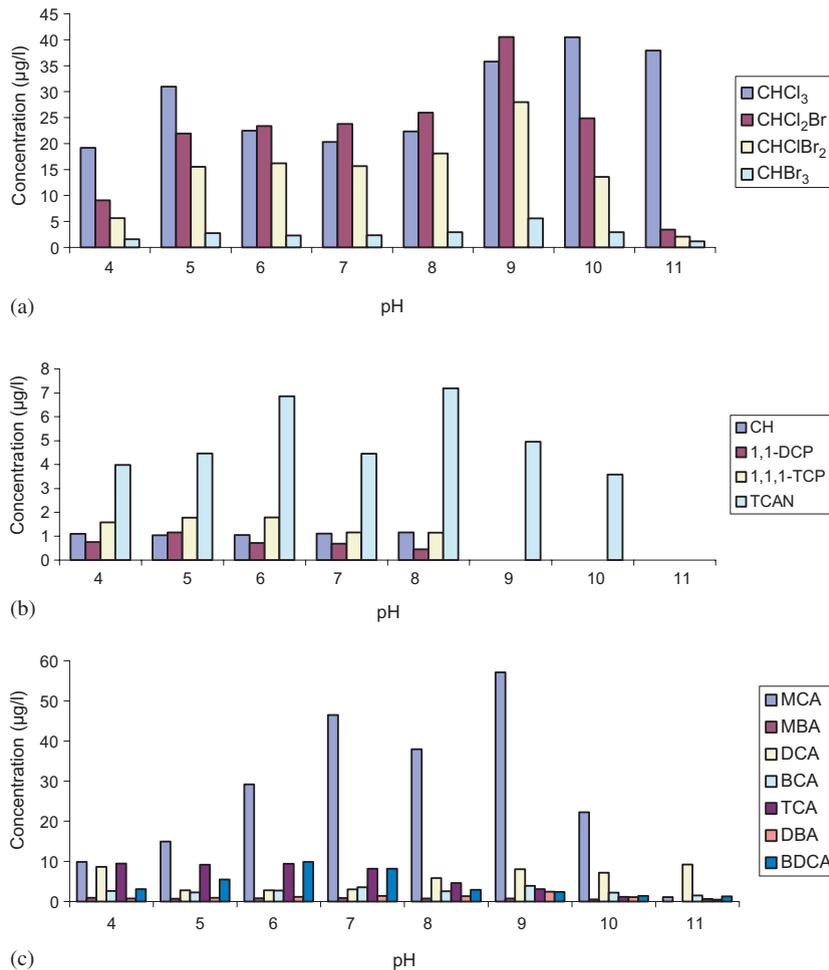


Fig. 1. Formation of (a) THM, (b) volatile CBPs, (c) HAAs in chlorinated water from Tsiknias river as function of pH (Cl dose 4 mg/l, reaction time 4 h).

rine dosages tested were 2 and 4 mg/l) were divided into 40-ml amber glass bottles with polypropylene screw caps and TFE-faced septa (Pierce 13075). The vials were carefully filled so that trapping of air bubbles inside was prevented. Then they were incubated at 21 °C until the desired contact times were fulfilled (the contact times tested were 0, 1, 2, 3, 4, 8, 16 and 24 h). Then, residual chlorine was measured according to the DPD colorimetric method (APHA, 1992) and the quenching agent for depletion of residual chlorine was added. Sodium sulfite

was used for the samples analyzed for THMs and other volatile CBPs and ammonium chloride for the samples analyzed for HAAs (100 mg/l of sample in both cases).

For THMs and other volatile CBPs, a modification of EPA Method 551.1, which includes liquid–liquid extraction (LLE) with MTBE was performed (Golfopoulos and Nikolaou, 2001). For HAAs, acidic methanol esterification (Nikolaou et al., 2002a) was used.

The determination of CBPs was carried out by use of a HP 5890 Series II Gas Chromatograph equipped with

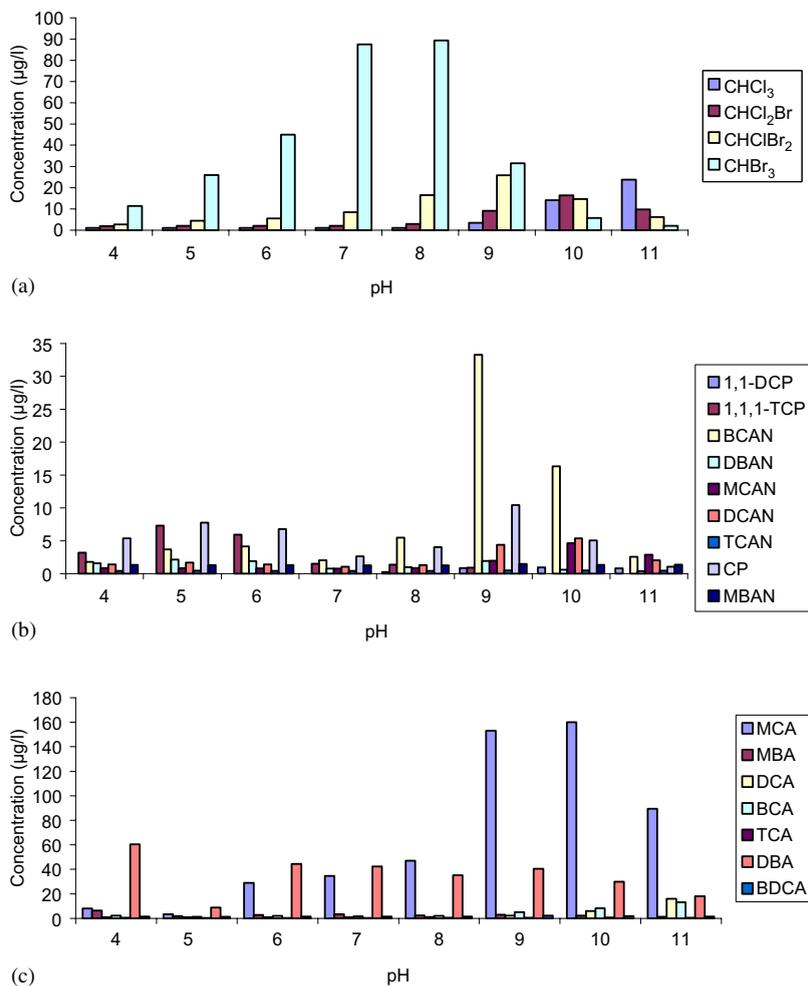


Fig. 2. Formation of (a) THM, (b) volatile CBPs, (c) HAAs in chlorinated water from Mylopotamos river as function of pH [Cl dose (a,b) 2 mg/l, (c) 4 mg/l, reaction time 4 h].

a  $^{63}\text{Ni}$  Electron Capture Detector (ECD). A capillary fused silica DB-1 column  $30\text{ m} \times 0.32\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$  film thickness was used. Injections were made in splitless mode, with helium as carrier gas and nitrogen as makeup gas. A Hewlett Packard Mass Selective Detector 5971 with a fused silica capillary HP-VOC ( $60\text{ m} \times 0.32\text{ mm} \times 1.8\text{ }\mu\text{m}$ ) was used for confirmatory purposes. The analytical conditions are presented elsewhere (Golfonopoulos and Nikolaou, 2001; Nikolaou et al., 2002a). UV absorbance measurements were carried out at 272 nm by use of a Cary 1E UV–visible spectrophotometer with 1-cm quartz cells.

## 2.2. Data analysis

The dependent variables (THMs and HAAs concentrations) were tested for normality and data transformation (log) was applied to approximate normal

distribution. The Kolmogorov–Smirnov (K–S) test was used to test the goodness-of-fit to the normal distribution (Zar, 1984). The relationships between the variables were examined by simple correlation. Multiple regression was applied to evaluate the statistically significant variables of the system, at significance level 0.05. The inclusion of each variable in the proposed model was based on the *t*-criterion (Ott, 1988). Methodological details about the model development are extensively discussed in past studies (Golfonopoulos et al., 1998; Golfonopoulos and Arhonditsis, 2002a).

## 3. Results and discussion

The characteristics of the river waters studied during sampling are shown in Table 1. The highest UV-272 absorbance was observed in river Mylopotamos (0.262

Table 2  
Correlation results for the proposed models

	pH	Time	logTHM	
<i>Model 1 (N = 112)</i>				
pH	1.000			
Time	0.000	1.000		
logTHM	0.227	0.435	1.000	
	pH	Time	Cl dose	logHAA
<i>Model 2 (N = 94)</i>				
pH	1.000			
Time	-0.023	1.000		
Cl dose	-0.012	0.128	1.000	
logHAA	-0.149	0.640	0.316	1.000
	pH	Cl dose	logTHM	
<i>Model 3 (N = 110)</i>				
pH	1.000			
Cl dose	-0.025	1.000		
logTHM	0.153	0.328	1.000	
	logpH	logtime	logCl dose	logHAA
<i>Model 4 (N = 76)</i>				
logpH	1.000			
logtime	-0.051	1.000		
logCl dose	-0.033	0.088	1.000	
logHAA	0.206	0.391	0.332	1.000

cm<sup>-1</sup>). In the same river significant concentrations of chloride and bromide ions were detected (143.9 and 2.5 mg/l respectively). It must be noted that the sampling point at this river is located near a saltwork.

None of the compounds studied was present in the raw water samples, but all of them were detected in chlorinated samples. The highest concentrations were detected in river Mylopotamos, due to the high organic matter content. Predominance of brominated species of CBPs, especially bromoform and DBA was observed in the same river, due to the presence of bromide ion. Statistical analysis of the results included analysis of variance (ANOVA), which showed that the factors pH, time and chlorine dose were statistically significant for the formation of CBPs in both rivers. Increase of THMs concentrations was observed with increasing pH. On the contrary, the volatile CBPs CH, 1,1-DCP and 1,1,1-TCP were formed only at pH < 8 and were favored from low pH. The influence of pH on HAAs formation is different for individual species. MCA and DCA are favored from high pH values, but the opposite is true for TCA and MBA. For BDCA, the optimum pH values were 6 and 7. The influence of reaction time was different for the different categories of CBPs, with THMs and HAAs favored from long reaction time, while volatile CBPs such as haloketones showing decreasing concentrations over time, due to hydrolysis and reactions with residual

chlorine. Increase of chlorine dose had positive influence on the formation of CBPs in all cases.

The formation of CBPs in chlorinated water from Tsiknias river as a function of pH is presented in Fig. 1 (Cl dose 4 mg/l, reaction time 4 h). The major species of CBPs formed during chlorination of water from Tsiknias river was MCA, followed by chloroform, dichlorobromomethane and dibromochloromethane. BCA, TCA, DCA, BDCA, bromoform, MBA, DBA, CH, 1,1-DCP, TCAN and 1,1,1-TCP were detected at lower concentrations. As regards THMs and other volatile CBPs, the maximum concentrations formed were 37.9 µg/l for chloroform, 40.6 µg/l for dichlorobromomethane, 28.0 µg/l for dibromochloromethane, 5.6 µg/l for bromoform, 7.2 µg/l for TCAN, 1.2 µg/l for CH, 1.2 µg/l for 1,1-DCP and 1.79 µg/l for 1,1,1-TCP. As regards HAAs, the maximum concentrations formed were 57.1 µg/l for MCA, 0.9 µg/l for MBA, 9.2 µg/l for DCA, 3.9 µg/l for BCA, 9.5 µg/l for TCA, 2.4 µg/l for DBA and 9.8 µg/l for BDCA. The predominance of chlorinated species over brominated ones occurs due to absence of bromide ion in this river water.

In chlorinated water from Mylopotamos river, the speciation of CBPs is entirely different, as shown in Fig. 2. Here, predominance of brominated species of CBPs was observed, due to high concentration of bromide ion. Moreover, a larger variety of CBPs (including CP,

Table 3  
Regression coefficients, standard errors and *t*-values for the variables included in the proposed models

	$\beta$	Standard error of $\beta$	<i>t</i> (108)	<i>p</i> -level
<i>Model 1</i>				
pH	0.326	0.017	17.792	0.000
pH <sup>2</sup>	-0.019	0.002	-10.572	0.000
Time	0.122	0.014	8.504	0.000
Time <sup>2</sup>	-0.004	0.001	-7.257	0.000
<hr/> <i>t</i> (90) <hr/>				
<i>Model 2</i>				
pH	0.333	0.026	12.466	0.000
pH <sup>2</sup>	-0.024	0.002	-10.917	0.000
Time	0.483	0.055	8.836	0.000
Cl dose	0.087	0.099	3.543	0.001
<hr/> <i>t</i> (106) <hr/>				
<i>Model 3</i>				
pH	-0.438	0.102	-4.311	0.000
logpH	7.535	1.624	4.638	0.000
Cl dose	-1.096	0.483	-2.267	0.025
Cl dose <sup>2</sup>	0.204	2.517	2.517	0.013
<hr/> <i>t</i> (72) <hr/>				
<i>Model 4</i>				
logpH	0.977	0.198	4.944	0.000
logtime	1.100	0.227	4.834	0.000
Time × Cl dose	-0.014	0.004	-3.309	0.001
logCl dose	1.586	0.314	5.040	0.000

BCAN, DBAN, MCAN and DCAN) were formed compared to chlorinated water from Tsiknias river, maybe due to the significantly higher organic matter content of Mylopotamos river (UV-272 0.262 cm<sup>-1</sup>) compared to Tsiknias river (UV-272 0.048 cm<sup>-1</sup>). The major species formed were bromoform, followed by MCA, DBA and dibromochloromethane. Chloroform, dichlorobromomethane, MCAN, DCAN, TCAN, CP, 1,1-DCP, 1,1,1-TCP, MBA, DCA, BCA, BDCA were detected at lower concentrations. As regards THMs and other volatile CBPs, the maximum concentrations formed were 23.8 µg/l for chloroform, 16.4 µg/l for dichlorobromomethane, 25.8 µg/l for dibromochloromethane, 89.3 µg/l for bromoform, 4.6 µg/l for MCAN, 5.4 µg/l for DCAN, 0.5 µg/l for TCAN, 33.3 µg/l for BCAN, 2.2 µg/l for DBAN, 10.4 µg/l for CP, 0.9 µg/l for 1,1-DCP and 7.31 µg/l for 1,1,1-TCP. As regards HAAs, the maximum concentrations formed were 160.0 µg/l for MCA, 3.5 µg/l for MBA, 15.9 µg/l for DCA, 13.1 µg/l for BCA, 0.6 µg/l for TCA, 60.4 µg/l for DBA and 2.1 µg/l for BDCA.

The development of multiple regression models for predicting the formation of total THMs and total HAAs for chlorinated water from Tsiknias river (models 1 and 2) and from Mylopotamos river (models 3 and 4) was based on the use of pH, reaction time and chlorine

dose. The concentrations of THMs and HAAs are expressed in µg/l, chlorine dose in mg/l and reaction time in h.

#### *Tsiknias river*

$$\log\text{THM} = 0.33\text{pH} - 0.02\text{pH}^2 + 0.12\text{time} - 0.004\text{time}^2 \quad (1)$$

$$\log\text{HAA} = 0.33\text{pH} - 0.02\text{pH}^2 + 0.48\text{time} + 0.09\text{Cl dose} \quad (2)$$

#### *Mylopotamos river*

$$\log\text{THM} = -0.44\text{pH} + 7.53\log\text{pH} - 1.10\text{Cl dose} + 0.20\text{Cl dose}^2 \quad (3)$$

$$\log\text{HAA} = 0.98\log\text{pH} + 1.10\log\text{time} - 0.01\text{time} \times \text{Cl dose} + 1.59\log\text{Cl dose} \quad (4)$$

The results of the K-S tests for the estimation of goodness-of-fit of the dependent variables of the models to the normal distribution showed that all dependent variables followed the normal distribution at significance level 0.05 after log-transformation.

The results of simple correlations for the examination of relationships between the variables are shown in Table 2. The regression coefficients ( $\beta$ ), the standard errors and the  $t$ -values for the variables included in the proposed models are presented in Table 3.

The developed models are second order, that is, they include all possible first and second-degree forms of the independent variables. Any variable  $x_i$  that appears as  $x_i^p$  is called a  $p$ th-degree term. The term  $x_i^p x_j^q$  is called a  $(p + q)$ th degree term (Ott, 1988).

Statistical examination showed that the residuals of the models follow the normal distribution (Draper and Smith, 1981).

The mean value of the residuals should be zero. The residuals should be evenly attributed above and below

zero, otherwise we should suspect a calculation error or that an additional variable should be added to the regression model (Zar, 1984). For the proposed models, the mean value of residuals is zero, and they are evenly distributed above and below the zero beeline, as presented in Fig. 3.

A comparison between predicted and observed values for all proposed models is presented in Fig. 4. It can be observed that the models provide a satisfactory estimation of the concentrations of CBPs formed. The percentage of observed values within  $\pm 20\%$  of predicted values ranged from 84% to 88%.

The number of observations  $N$ ,  $F$ ,  $R^2$ , standard error of estimate and Durbin–Watson estimate for the proposed models are shown in Table 4. All models are

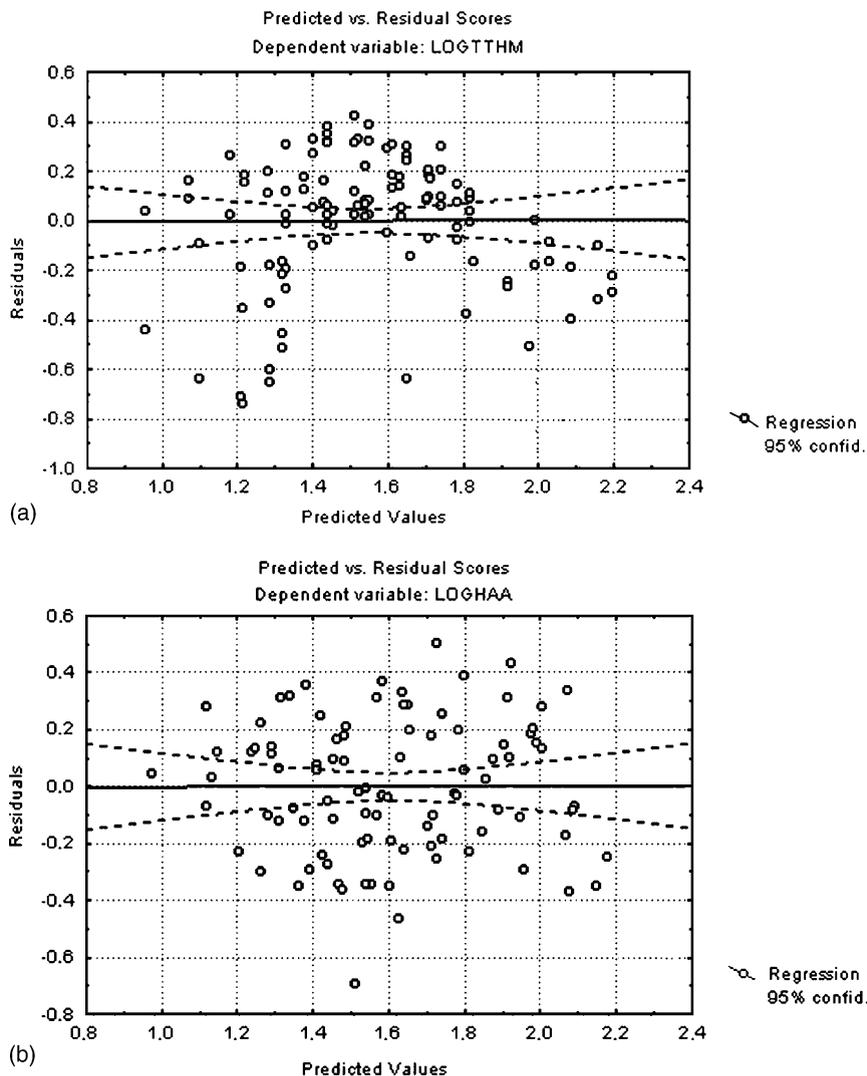


Fig. 3. Plots of residuals versus predicted values for (a) model 1, (b) model 2, (c) model 3 and (d) model 4.

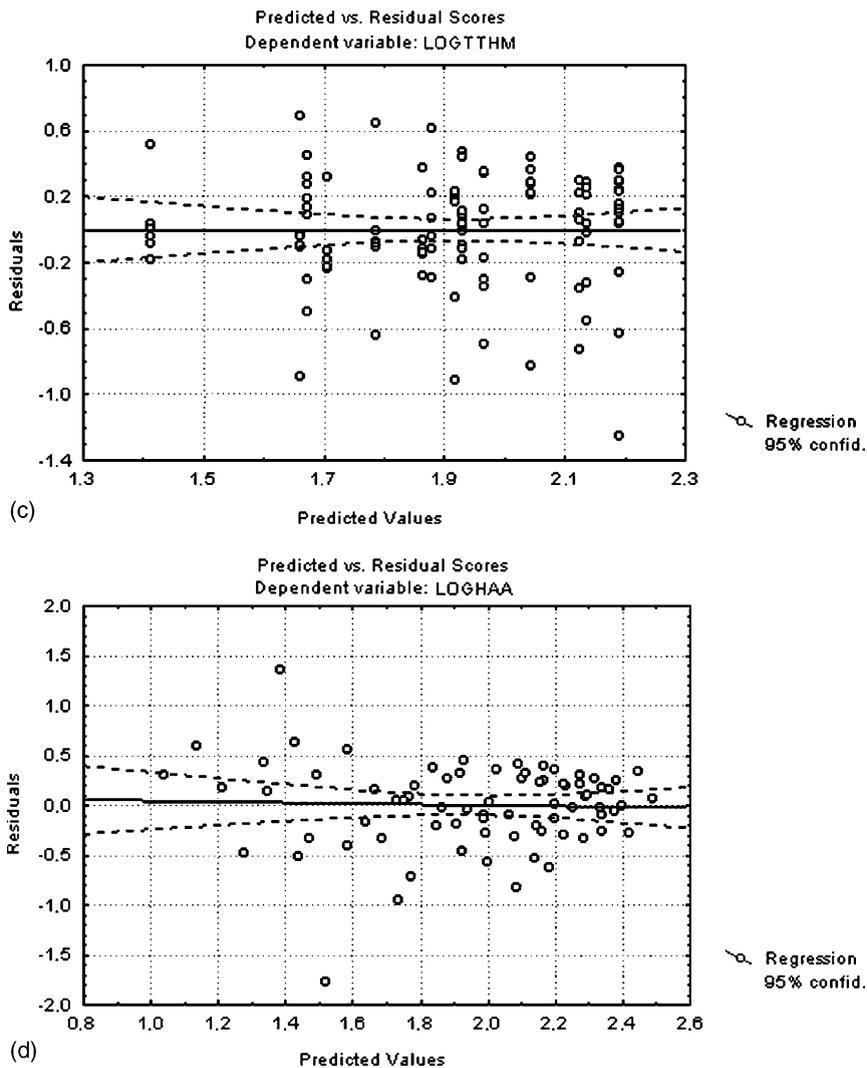


Fig. 3 (continued)

statistically significant and the values of the Durbin–Watson statistic indicate the weak serial correlation of the residuals. The regression coefficients ( $r^2$ ) were ranging from 0.28 to 0.58, which is a satisfactory level of explanation of the observed variability, but certainly lower than those reported in previous studies (Golfinoopoulos et al., 1998; Golfinoopoulos and Arhonditsis, 2002b). The different water quality characteristics of the present study, especially in Mylopotamos river (high organic matter and bromide content), are likely to be the main cause for these discrepancies. It seems that under these conditions the formation of THMs and HAAs in water has a more stochastic character, which is difficult to be described by the conventional regression techniques.

*Future perspectives.* The development of reliable models is increasingly recognized as an essential methodological basis for predicting CBPs formation. A number of modeling studies have been published over the last decade which in general can be divided into two groups; linear or non-linear models statistically fit to data (e.g., Amy et al., 1987; Rathbun, 1996; Chapra et al., 1997; Garcia-Villanova et al., 1997) and mechanistic models that usually attempt to simulate reaction kinetics (e.g., Nokes et al., 1999; Clark et al., 2001). There are well-founded arguments in support of each rationale and we do not intend with the present paper to argue in favour of one of these two approaches. In the past, we attempted to develop both statistical (Golfinoopoulos et al., 1998; Golfinoopoulos and Arhonditsis, 2002a; Nikolaou et al.,

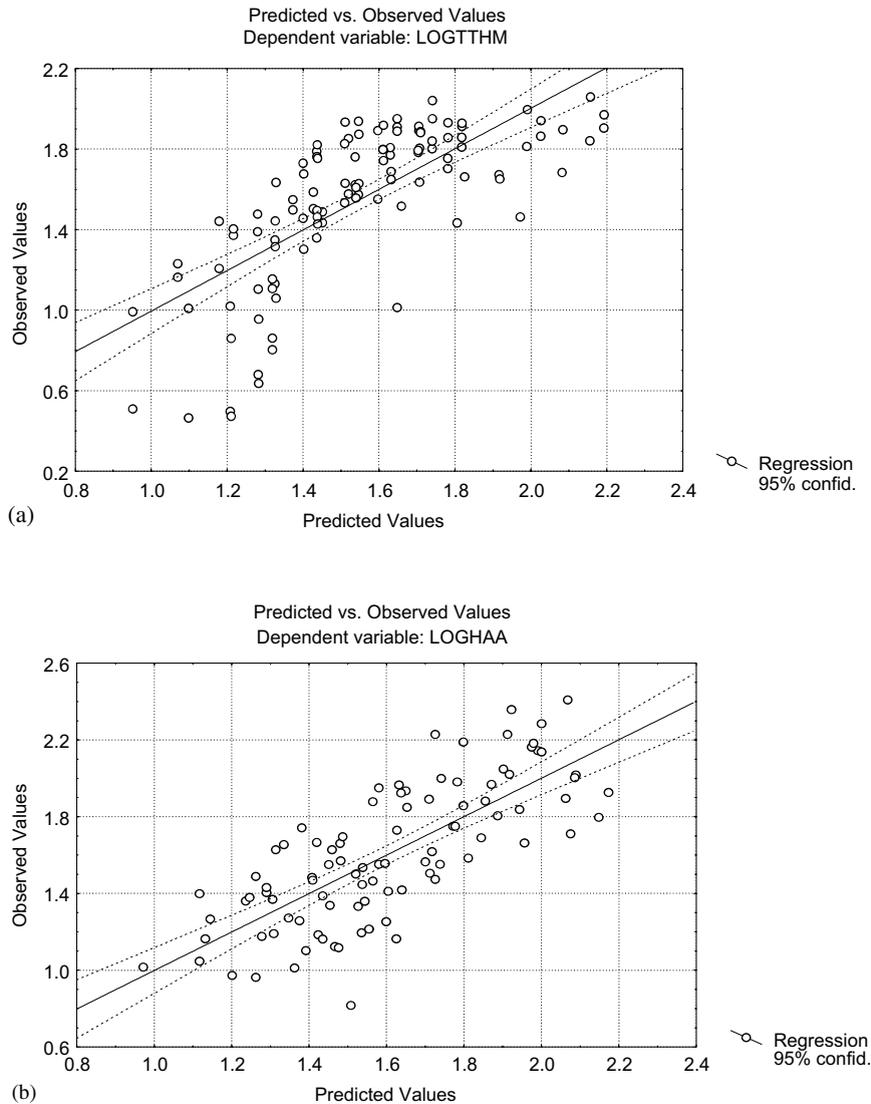


Fig. 4. Comparison between predicted and observed values for (a) model 1, (b) model 2, (c) model 3 and (d) model 4.

2002b) and mechanistic (Golfinoopoulos and Arhonditsis, 2002b) models with equivocal results. For example, the multiple regression model by Golfinoopoulos and Arhonditsis (2002a) resulted in a satisfactory agreement between observed and predicted values for both TTHM ( $r^2 = 0.52$ ) and individual THM species ( $r^2 > 0.51$ ) concentrations. In addition, the fairly complex-mathematical formulation of the model was almost identical to a former construct which was considered as an evidence for potential generalisation of the models in areas with similar climatic conditions to those of the Greek region. However, when this study attempted to validate the models against an independent data-set, the  $r^2$  values were significantly lower (0.37–0.54) and missed several highs (see

Fig. 5 of the paper). On the other hand, Golfinoopoulos and Arhonditsis (2002b) driven by the need of realistically reproducing water treatment plant processes, proposed a quasi-equilibrium approach that also gave satisfactory results. The basic flaw of this study is that the best fit was found by a stoichiometric ratio for total halogen: organic substrate: TTHM (2.5:3:1) that deviates from what is usually suggested from other studies. We do not mean to be overly critical with our work but just to indicate the discrepancies and inaccuracies that underlie both the modeling approaches. We agree with viewpoints that it is still quite risky to characterize the existing models capable for consistently predicting CBPs levels or formation potentials in water treatment plants (Clark et al., 2001).

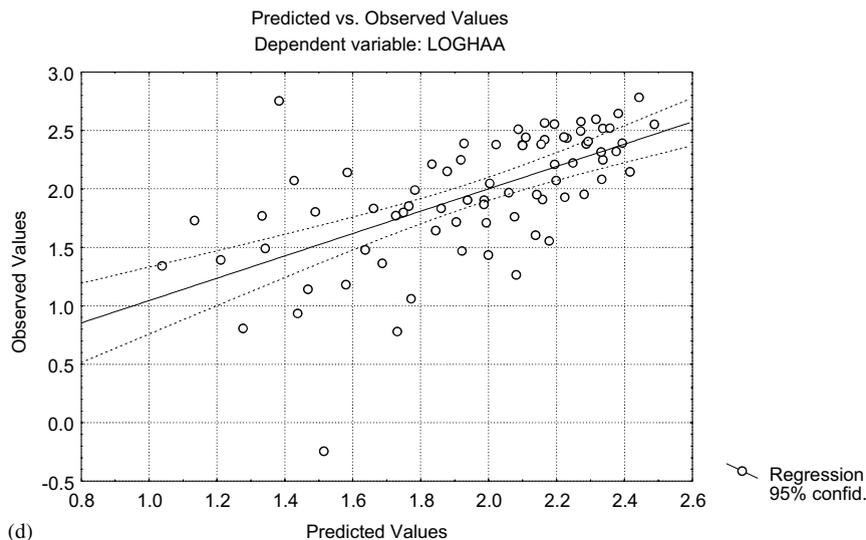
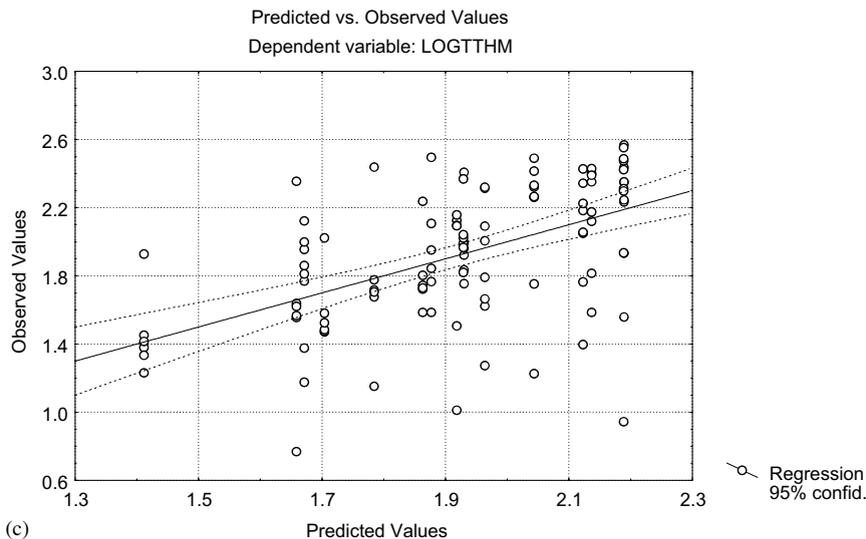


Fig. 4 (continued)

Table 4  
Statistical evaluation of the proposed models for THMs and HAAs concentrations

Model number	<i>N</i>	<i>F</i>	<i>R</i> <sup>2</sup>	Standard error of estimate	Durbin–Watson estimate
1	112	$F(4, 108) = 981.76 > F_{0.05} = 2.45, F_{0.01} = 3.48$	0.53	0.266	1.96
2	94	$F(4, 90) = 1076.1 > F_{0.05} = 2.45, F_{0.01} = 3.48$	0.58	0.241	1.89
3	110	$F(4, 106) = 863.40 > F_{0.05} = 2.45, F_{0.01} = 3.48$	0.28	0.344	2.23
4	76	$F(4, 72) = 399.27 > F_{0.05} = 2.53, F_{0.01} = 3.65$	0.38	0.434	2.07

An alternative approach would be the introduction of the dynamic regression models with variant vector of parameters. The basic feature that distinguishes these

models from the classical ones is that the regression parameters are allowed to vary through time (or case). It has been proved from previous studies that the variation

of model parameters (regardless if it is dynamic or regression modeling) can give insight and assign different weights to the used predictors (Golfinopoulos and Arhonditsis, 2002b). Moreover, these case-dependent values and the consequent ranges can be used as a direct uncertainty analysis for the modeling approaches and thus enabling the users to understand their validity and potential applicability. Additional benefits can also be gained from methodological frameworks developed in other field areas, such as aquatic ecosystems research, that combine simple mechanistic equations with Bayesian analysis (e.g., Borsuk et al., 2001). By incorporating prior knowledge and replacing the classical point estimates with full parameter and predictive distributions, both theoretical understanding and model precision can be improved. Given the intricate nature and the multiple synergistic effects that characterize the CBPs formation these frameworks can be very useful for developing general methodological tools that predict the formation of THMs and HAAs based on raw water characteristics and disinfection practices and assist the utilities' operators to conform with the legislative measures.

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