

Modelling of haloacetic acid concentrations in a United Kingdom drinking water system

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ABSTRACT

Haloacetic acids (HAAs) are formed during the chlorination of water containing organic matter but predictive models for their formation are not well established at present and have not been applied to UK water systems. In this paper two different modelling approaches have been applied and evaluated to a selected UK drinking water system. The first approach involved the development of statistical predictive models for the HAA formation by using multiple linear regression with appropriate water quality and operational parameters obtained from sampling, and the second approach employed the simulated distribution system (SDS) test. Statistically significant predictors were trihalomethane (THM) levels, pH, temperature, total chlorine total organic carbon, UV_{254} , bromide concentration and residence time, but the importance of each varied with HAA species. The models that generally explained most of the variance of individual and total HAAs included THMs as a predictor variable. The use of the SDS-HAA test included quantification of individual HAA species. The concentration of total HAA and individual compounds in the SDS test and field samples were comparable immediately after chlorination, but with increasing residence time the concentration of HAAs in the selected water distribution system were greater than those found in the SDS test.

Key words | disinfection by-products, distribution system, drinking water, haloacetic acids, multiple linear regression models

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INTRODUCTION

Disinfection is an important process in the treatment of drinking water supplies as it removes or inactivates pathogenic microorganisms responsible for waterborne disease such as cholera and dysentery (Uyak *et al.* 2005). Chlorination is a widely used disinfection method because of its efficient and cost-effective properties. However, disinfection by-products (DBPs) are generated during water disinfection due to the reaction of chlorine with natural organic matter (NOM) contained in the raw water and in treated water at the point of final disinfection. Because of their potential health risks, four groups of DBPs are regulated currently under the United States Environmental Protection Agency (USEPA) Stage 1 Disinfectant and Disinfection By-products (D/DBP

Rules (USEPA 1998). These four groups are trihalomethanes (THMs), haloacetic acids (HAAs), chlorite and bromate. The maximum contaminant levels (MCLs) established by the D/DBP Stage 1 Rules are 80 $\mu\text{g}/\text{l}$ for total THMs, 60 $\mu\text{g}/\text{l}$ for HAA_5 , 1 mg/l for chlorite and 10 $\mu\text{g}/\text{l}$ for bromate. The term HAA_5 describes the group of the following five HAA compounds, monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). In the United Kingdom HAA compounds are not regulated, but there is considerable interest in their occurrence and formation since regulation may be introduced soon; recently a standard of 80 $\mu\text{g}/\text{l}$ for HAA_9 has been suggested for the

future revision of the EU Drinking Water Directive (DHI 2008). The term HAA₉ describes the group of nine HAA compounds comprising the HAA₅, and the following four compounds, bromochloroacetic acid (BCAA), chlorodibromoacetic acid (CDBAA), bromodichloroacetic acid (BDCAA), and tribromoacetic acid (TBAA).

HAA occurrence in chlorinated water may vary significantly based on season and geographical location in the distribution system (LeBel *et al.* 1997; Sérodes *et al.* 2003; Rodriguez *et al.* 2004). These variations are due to changes in raw and treated water qualities as well as operational parameters related to chlorination. In terms of water quality, the fractions of NOM (i.e. hydrophobic/hydrophilic and acid/neutral/base) constitute important precursors for the formation of HAAs (Marhaba & Van 2000; Chang *et al.* 2001; Liang & Singer 2003; Kim & Yu 2005, 2007). Generally, the hydrophobic fraction has been reported to be more reactive in producing HAAs than the corresponding hydrophilic fraction. The operational and other water quality parameters which influence the formation of HAAs include water temperature, pH, bromide concentration, chlorine dose, and contact time (Liang & Singer 2003; Sérodes *et al.* 2003; Rodriguez *et al.* 2004).

Finished drinking water generally takes hours or days to reach its customers, especially in a large distribution system. Residual chlorine may react with various substances in the water and on the pipe walls resulting in increases in HAA concentrations with water age through a distribution system (Rodriguez *et al.* 2004). Moreover, HAA species may undergo a different fate during this period, in which some may be degraded by bacteria in bio-films on the internal surfaces of pipes (McRae *et al.* 2004), some may react with the pipe material (i.e. cast iron) (Hozalski *et al.* 2001), and some may decompose with the changing aqueous conditions due to their unstable chemical properties (Cowman & Singer 1996; Zhang & Minear 2002).

In recent years, research studies have attempted to develop statistical predictive models for the formation of DBPs in water, either from data generated from full-scale water supply systems or at laboratory-scale using controlled chlorination conditions (Amy *et al.* 1998; Goufopoulos *et al.* 1998; Rodriguez *et al.* 2003; Villanueva *et al.* 2003; Nikolaou *et al.* 2004; Uyak *et al.* 2007; Ghebremichael *et al.* 2008). Most of the work has been focused on the

formation of THMs, and so far relatively little has been reported on HAAs (Table 1), and nothing involving UK drinking waters and water treatment conditions (Chowdhury *et al.* 2009). Furthermore, the simulated distribution system (SDS) test method, which was developed specifically to estimate the THM formation, has been used in practice and research to simulate other DBPs concentrations in water supply networks (Koch *et al.* 1991). All these predictive models are useful for operational purposes during water treatment and water quality management, for the evaluation of water treatment facilities, for exposure assessment in epidemiological studies and health risk assessment, and for estimating the benefits and impacts of DBP regulations.

In this paper we describe an analysis of data obtained from a selected UK water system for the following objectives: (i) the development of statistical predictive models for the formation of total HAAs and individual HAA species based on appropriate water quality and operational parameters; (ii) the evaluation of bench-scale SDS tests to predict HAA formation by correlating the results with observed values from the water distribution systems. Both approaches, although different, offer practical methods of predicting HAA formation in water supply.

MATERIALS AND METHODS

Description of water treatment works

We have previously described the occurrence of HAAs in three water supply systems in the UK (Zhang *et al.* 2010) and the data used for this modelling study are from one of them, namely, system C. System C, which has a flow capacity of 48 ML/day, treats water from two upland reservoirs and the treatment process consists of coagulation/flocculation, sedimentation, first stage filtration, and a second stage filtration with pre-chlorination (for manganese removal and disinfection).

Sampling procedure and field measurements

The sampling program for the development of the statistical predictive models was carried out during the period of April

Table 1 | Summary of HAA predictive models

Data source	Models ^a	N	r ²	References
Laboratory	MCAA = 1.634(TOC) ^{0.755} (Br ⁻ + 0.01) ^{-0.085} (pH) ^{-1.124} (D) ^{0.509} (t) ^{0.300}	81	0.820	Montgomery (1993)
	DCAA = 0.605(TOC) ^{0.291} (UV) ^{0.726} (Br ⁻ + 0.01) ^{-0.568} (pH) ^{-1.124} (D) ^{0.48} (t) ^{0.239} (T) ^{0.665}	172	0.970	
	TCAA = 87.182(TOC) ^{0.355} (UV) ^{0.901} (Br ⁻ + 0.01) ^{0.679} (pH) ^{1.732} (D) ^{0.881} (t) ^{0.264}	172	0.980	
	MBAA = 0.176(TOC) ^{1.664} (UV) ^{-0.624} (Br ⁻) ^{0.795} (pH) ^{-0.927} (t) ^{0.145} (T) ^{0.45}	79	0.800	
	DBAA = 84.945(TOC) ^{-0.62} (UV) ^{0.651} (Br ⁻) ^{1.075} (D) ^{-0.2} (t) ^{0.12} (T) ^{0.657}	81	0.950	
Field	CDBAA = -0.119 + 0.159CHClBr ₂	18	0.967	Villanueva et al. (2003)
	DCAA = 1.534 + 0.566CHCl ₂ Br - 0.258CHBr ₃	18	0.939	
	TBAA = -0.13 + 0.0898CHBr ₃	18	0.922	
	BCDAA = -0.154 + 0.131CHCl ₃ + 0.277CHClBr ₂ - 0.125CHBr ₃	18	0.911	
	DBAA = -0.046 + 0.143CHClBr ₂ + 0.192CHBr ₃	18	0.876	
	BCAA = 1.045 + 0.409CHClBr ₂ - 0.212CHBr ₃	18	0.844	
	MBAA = 0.442 + 0.0459CHBr ₃	18	0.680	
	TCAA = 1.269 + 0.375CHCl ₃	18	0.658	
	MCAA = -0.028 + 0.0399CHBr ₃	18	0.573	
Laboratory	HAA = 2.720(t) ^{0.295} (D) ^{0.458} (TOC) ^{0.653}	53	0.890	Sérodes et al. (2003)
	HAA = 1.330(t) ^{0.102} (T) ^{0.255} (D) ^{0.102} (TOC) ^{2.612}	55	0.800	
	HAA = -8.202(t) ^{0.364} (D) ^{1.053} (TOC) ^{4.869}	51	0.920	
Field	MCAA = 0.45(t) ^{-0.009} (T) ^{0.573} (pH) ^{-0.279} (D) ^{0.397} (DOC) ^{0.173} (Br ⁻) ^{0.029}	738	0.140	Amy et al. (1998)
	MBAA = 6.21 × 10 ⁻⁵ (t) ^{-0.090} (T) ^{0.707} (pH) ^{0.504} (D) ^{0.754} (DOC) ^{-0.584} (Br ⁻) ^{-1.100}	738	0.430	
	DCAA = 0.30(t) ^{0.218} (T) ^{0.465} (pH) ^{0.200} (D) ^{-0.379} (DOC) ^{1.396} (Br ⁻) ^{-0.149}	738	0.830	
	TCAA = 92.68(t) ^{0.180} (T) ^{0.299} (pH) ^{-1.627} (D) ^{0.531} (DOC) ^{1.152} (Br ⁻) ^{-0.229}	738	0.870	
	BCAA = 5.51 × 10 ⁻³ (t) ^{0.220} (T) ^{0.379} (pH) ^{0.581} (D) ^{0.522} (DOC) ^{0.463} (Br ⁻) ^{0.667}	738	0.760	
	DBAA = 3.59 × 10 ⁻⁵ (t) ^{0.095} (T) ^{0.360} (pH) ^{-0.001} (D) ^{0.673} (DOC) ^{-1.066} (Br ⁻) ^{-2.052}	738	0.770	
HAA = 9.98(t) ^{0.178} (T) ^{0.387} (pH) ^{-0.855} (D) ^{0.443} (DOC) ^{0.955} (Br ⁻) ^{-0.031}	738	0.870		
Laboratory	HAA = 10 ^{0.874} (D) ^{0.351} (pH) ^{-1.2485} (t) ^{0.172} (SUVA) ^{-0.469}	-	0.610	Uyak et al. (2007)

^aNomenclature: D = chlorine dose, T = temperature, t = reaction time.

2007 to January 2008, approximately corresponding to one set of samples for each of four distinct seasons (spring, summer, autumn and winter). Water samples were collected at three locations in the water treatment works (one sample at each), namely: (i) the raw water before coagulation; (ii) after the first stage filtration (treated but unchlorinated); (iii) after chlorination/second stage filtration (final water). To monitor the values and approximate distribution of HAAs in the distribution system, 15 samples were taken from three separate water supply zones; the zones were spatially separated to correspond to a short, medium and long flow residence times in the distribution system. Thus, overall 18 samples were taken for each of the four seasons. Water samples were collected in 500 ml amber glass bottles with ammonium chloride (NH₄Cl) at the concentration of 100 mg/l. The samples were filled to just overflowing without flushing out the NH₄Cl. When sampling from a water tap, the aerator was removed, and the system was allowed to flush until the water

temperature had stabilized. After collecting the sample, the bottle was sealed and agitated by hand for 15 s.

Once collected, samples were refrigerated at 4 °C and maintained at a temperature of ≤10 °C during shipment. Parameters such as pH, temperature, free chlorine concentration, and total chlorine concentration were measured on site, and UV₂₅₄ absorbance, total organic carbon (TOC) and Br⁻ concentrations were subsequently determined in the laboratory; all tests were carried out according to standard methods (APHA 1998). The THM concentrations were analysed by the water company using standard methods for the UK for samples taken on the sampling day (Standing Committee of Analysts 1981, 1985).

Determination of HAAs

HAA analysis was performed using EPA Method 552.3 (USEPA 2003): 40-ml aqueous sample was adjusted to a

pH of 0.5 or less and extracted with 4 ml of methyl-tert-butyl-ether (MTBE) containing internal standard (1,2,3-trichloropropane). The haloacetic acids that had been partitioned into the organic phase were then converted to their methyl esters by the addition of acidic methanol followed by heating for 2 h. The solvent phase containing methylated haloacetic acids was separated from acidic methanol by adding 7 ml of concentrated aqueous solution of Na₂SO₄, and the extract was neutralized by the addition of a saturated solution of NaHCO₃. The target analytes were identified and quantified by capillary column gas chromatography using an electron capture detector (GC/ECD). All sample analysis was carried out in duplicate; further details can be found elsewhere (Zhang *et al.* 2010).

SDS-HAA test

The SDS test (APHA 1998) was performed by a bench-top procedure in which treated water samples were chlorinated under site-specific conditions of time, temperature, pH, and chlorine dose or residual that represented the conditions of the actual distribution system.

In this aspect of the study, water samples from system C on one day were collected after physical/chemical treatment but before chlorination. The SDS test was conducted for approximately 7 days under the following conditions which were identical to those of the system at the same time: pH 7.0, temperature 21 °C, and chlorine dose 1.7 mg/l. All samples and their duplicates were chlorinated in 250 ml amber bottles with PTFE-lined screw cap, stored headspace-free in the dark. Then water samples were collected headspace-free into 40 ml amber vials containing NH₄Cl as a quenching agent after incubation times of 0 h, 2 h, 12 h, 1 day, 2 days, 3 days, 4 days, 5 days, 6 days and 7 days for HAA analysis, which was described previously. These incubation times were in addition to an initial 5 h period after the chlorine dose, to simulate the system chlorination contact time (before the water passed into distribution) which was 5 h on the day. Measurements of free residual chlorine were conducted at the same time in accordance with Standard Method 4500-Cl F (APHA 1998). On the same sampling day, additional water samples were collected from the point where water leaves the treatment works (final water), and three others from each of the three

water supply zones at 3, 6.5 and 9 h residence time (values provided by the water company), to compare the HAA concentrations with those from the SDS test.

Data analysis and model development

Multiple linear regression was used to estimate the relationship between HAA concentrations and predictor variables (Menard 1995). The relationship between variables can be described using an equation in the following form:

$$Y = \beta_0 + \sum_{i=1}^m \beta_i X_i$$

where Y is the dependent variable, X_i represents the independent variables with m denoting the number of independent variables considered, β_0 the intercept and β_i the partial slope coefficients providing a partial explanation or prediction for the value of Y . The linear regression model coefficients are estimated using the ordinary least squares method which results in a line that minimizes the sum of squared vertical distance from the observed data points to the line. In this study, the model developed was based on the HAA concentrations from the field measurements in the four seasons sampling campaign. The potential explanatory variables were water pH, temperature, free chlorine, total chlorine, TOC, UV₂₅₄ absorbance, specific UV absorbance (SUVA), Br⁻, residence time and seasonal factors.

RESULTS AND DISCUSSION

HAA formation

During the model study period, a total of 72 samples were collected from system C and its distribution network. The statistical summary of water quality parameters for the distribution network samples is shown in Table 2. The specific UV absorbance (SUVA), defined as the UV absorbance per metre at 254 nm divided by the dissolved organic carbon concentration (DOC), has been demonstrated to be a good predictor of the aromatic carbon content of the NOM and the DBP formation potential of the water (Chin *et al.* 1994; Liang & Singer 2003). The mean SUVA value of the water

Table 2 | Quality parameters of water samples from the distribution network

Variables	Mean	Std	Min	Max
pH	7.4	0.03	6.7	7.9
Temp (°C)	13.1	0.4	7.3	18.9
CLFR ^a (mg/l)	0.5	0.02	0.1	0.8
CLTO ^b (mg/l)	0.6	0.02	0.1	0.9
TOC (mg/l)	3.7	0.3	1.2	10.1
UV ₂₅₄ (Abs/cm)	0.02	0.001	0.01	0.04
SUVA (l/mg m)	0.9	0.1	0.1	2.1
Br ⁻ (mg/l)	0.01	0.001	n.d. ^c	0.04
Residence time (h)	12.4	1.9	0.0	46.0
TTHM (µg/l)	30.3	1.1	16.5	47.3

^aFree Chlorine.^bTotal Chlorine.^cn.d. – not detected.

samples in this study was 0.9 l/(mg m). Table 3 shows the nine individual and total HAA concentrations measured. HAAs were not detected in unchlorinated water (i.e. raw, and treated but not chlorinated water). Only five HAAs were detected in the water samples that had received chlorination; DCAA, TCAA, BCAA, BDCAA and DBAA. This was also the case with the other two water supply systems that were sampled as part of the overall HAA occurrence study (Zhang *et al.* 2010). Compared with a previous study carried out in the UK (Malliarou *et al.* 2005), where a mean concentration of total HAA ranging from 35.1–94.6 µg/l and a

Table 3 | Individual and total HAA concentrations (µg/l) measured during the sampling period ($n = 64$)

	LOD ^a (µg/l)	Average (SD)	Max	Min	Median
TCAA	0.03	9.8 (2.8)	18.5	4.1	9.0
DCAA	0.12	6.8 (2.7)	15.0	3.1	6.8
BDCAA	1.32	2.7 (1.7)	5.3	0.0	3.3
BCAA	0.60	1.7 (0.8)	3.2	0.6	3.3
DBAA	0.16	0.4 (0.2)	0.7	0.1	0.3
MCAA	2.17	n.d. ^b			
MBAA	0.34	n.d.			
CDBAA	0.69	n.d.			
TBAA	3.80	n.d.			
THAA	–	21.3 (6.9)	41.0	11.1	20.6

^aLOD – limit of detection.^bn.d. – not detected.

maximum concentration of 244 µg/l were reported, the total HAA concentrations found in this study were relatively low (average value of 21.3 µg/l, with a maximum value of 41.0 µg/l and a minimum value of 11.1 µg/l). Since the previous study was based on individual samples (approximately one per zone) taken quasi-randomly from many water supply zones (58) across three large regions of England in a 2 week period, there is insufficient information to explain the reason for the differences in the observed HAA concentrations. The major species of HAAs formed during the sampling period were TCAA and DCAA (Table 3), where the sum of the two species represented over 70% of the total HAAs; TCAA and DCAA also comprised the majority of the total HAA (THAA) concentration in the previous study (Malliarou *et al.* 2005).

Correlations of HAA with other parameters

The results show that there were moderate negative correlations between total and free chlorine levels and THAA levels, and weak to moderate positive correlations between pH, temperature UV₂₅₄ and THAA levels (Table 4). Correlations between TOC, Br, SUVA and residence time and THAA levels were weak, but a strong relationship ($r = 0.81$) was obtained between THAA and TTHM. Total THM levels have been used previously as a surrogate for HAA levels (Nissinen *et al.* 2002; Villanueva *et al.* 2003). However, this may not always be appropriate, as a moderate or poor relationship was observed by others in some cases (Chin *et al.* 1994; Rodriguez *et al.* 2004). The observed correlations are difficult to explain in terms of fundamental mechanisms, given the complex nature of the factors involved and their interactions. However, useful background information can be found elsewhere concerning the mechanisms of HAA formation (Xie 2004; Huang 2010).

Statistical predictive HAA models

Statistical predictive models were constructed for HAAs including, and excluding, THM levels. Only statistically significant predictors, or predictors that changed the explained variance by more than 5% are given (Table 5; explained variance is the proportion to which a mathematical model accounts for the variation of a given data set). In

Table 4 | Correlation matrix for water quality and operational parameters

	THAA	pH	Temp	CLFR	CLTO	UV ₂₅₄	TOC	SUVA	Br ⁻	TTHM	resT
THAA	1.00										
pH	0.35	1.00									
Temp ^a	0.46	0.24	1.00								
CLFR ^b	-0.54	-0.20	-0.63	1.00							
CLTO ^c	-0.54	-0.19	-0.65	0.99	1.00						
UV ₂₅₄	0.40	0.40	0.51	-0.30	-0.31	1.00					
TOC	0.10	-0.23	-0.56	0.09	0.11	-0.26	1.00				
SUVA	0.19	0.37	0.72	-0.30	-0.31	0.77	-0.76	1.00			
Br	0.14	0.27	0.23	-0.35	-0.31	0.29	0.02	0.24	1.00		
TTHM	0.81	0.40	0.50	-0.69	-0.69	0.34	0.05	0.16	0.31	1.00	
resT ^d	0.15	-0.29	0.25	-0.31	-0.32	-0.06	0.08	-0.04	-0.03	0.22	1.00

^aTemperature.^bFree chlorine.^cTotal chlorine.^dResidence time.

contrast to various other studies (Sadiq & Rodriguez 2004; Table 1), we did not log-transform the HAA or water quality levels because they generally showed a normal distribution and when plotting the HAA levels against the predictor variables, they generally showed a linear relationship (Appendix 1, available online at <http://www.iwaponline.com/jws/060/047.pdf>). The statistical predictive models explained between 31% and 70% of the variation in HAA levels, with models including THMs as predictors showing the highest explained variance (53–70%), and without THMs lower variance (31–61%). Statistically significant predictors were THM levels, pH, temperature, total chlorine, total organic carbon, UV₂₅₄, bromine and residence time, but the importance of each varied with HAA species. The models that generally explained most of the variance of individual and total HAAs included THMs as a predictor variable, which is not surprising given the high correlation between total HAAs and total THMs; they also share the same predictors.

For models without THMs as a predictor, a statistically significant trend of increasing HAAs with pH was observed (in general, but excluding BDCAA). This is opposite to what Liang & Singer (2003) reported because they observed that increasing pH from 6 to 8 had little effect on the formation of the monohaloacetic acids (XAA) and dihaloacetic acids (X₂AA) species, but significantly decreased the formation

of trihaloacetic acids (X₃AA) species. However, Uyak *et al.* (2007) found that TCAA formation increased with pH up to pH 8 in one of the three treatment plants studied.

Temperature was a statistically significant predictor for THAA, TCAA and DCAA but not the other HAA species. A general observation from previous studies shows that with increasing water temperature, the amount of HAA formed through the disinfection process increases accordingly, which may be due to fast formation reactions (Williams *et al.* 1997). Seasonal variations in temperature can also affect the reaction rate. However, increasing temperature also accelerates the decomposition of HAAs (Zhang & Minear 2002).

The predictive value of total chlorine, TOC, UV₂₅₄, Br and residence time for the HAA species was less consistent and varied considerably by species, and this was evident when considering the correlation coefficients (Table 4). These inconsistent and counterintuitive results may be partly explained by the method employed since it has some limitations, such as the need for many observations, and the complexity of the system and interaction of different parameters that makes it harder to model what is happening in the real world. Furthermore, we have focused mainly on statistically significant results. Also, we only tried to model one water supply system and perhaps the lack of variability in the parameters may have limited the possibility to observe

Table 5 | Partial scope coefficients (β) for HAA regression models (95% confidence interval shown in parenthesis)

Determinants	TCAA		DCAA		BDCAA ^a	BCAA		DBAA		THAA	
	With TTHM	Without TTHM	With TTHM	Without TTHM		With TTHM	Without TTHM	With TTHM	Without TTHM	With TTHM	Without TTHM
Intercept (β_0)	-5.2 (-8.9, -1.6)	-31.3 (-56.7, -6)	0.8 (-0.8, 2.3)	-42.7 (-63.4, -21.9)	1.2 (0.2, 2.3)	0 (-0.9, 1)	-5.6 (-10.9, -0.4)	-1.3 (-2.4, -0.1)	-1.8 (-3.1, -0.5)	-2.6 (-9.5, 4.3)	-83.5 (-131.9, -35.1)
pH		4.3 (1.1, 7.5)		5.7 (2.9, 8.5)			1.1 (0.4, 1.8)	0.2 (0, 0.3)	0.3 (0.1, 0.5)		10.5 (3.9, 17)
Temperature (°C)	0.5 (0.2, 0.8)	0.7 (0.4, 1.1)		0.5 (0.3, 0.8)						0.6 (0.02, 1.1)	1.6 (1.1, 2.2)
CLTO (mg/l)		-5.2 (-9.6, -0.9)			-1.5 (-2.8, -0.1)	1.5 (0.7, 2.3)		0.4 (0.2, 0.6)			
TOC (mg/l)	0.4 (0,0.7)	0.8 (0.4, 1.2)		0.5 (0.2, 0.8)	0.3 (0.2, 0.4)					0.6 (0, 1.3)	1.8 (1.1, 2.5)
UV254 (Abs/cm)			59.3 (8.9, 109.7)						-9.2 (-12.8, -5.6)		
Br ⁻ (mg/l)			-108.1 (-153.3, -62.8)	-100.8 (-157.2, -44.4)	101.6 (74.1, 129.1)	-60.6 (-73.4, -47.8)	-60.8 (-75.3, -46.4)	-9.7 (-12.8, -6.6)		-100.4 (-200, 3.6)	
TTHM (μ g/l)	0.2 (0.2, 0.3)		0.2 (0.2, 0.3)			0.1 (0, 0.1)		0.01 (0.01, 0.02)		0.5 (0.4, 0.7)	
<i>R-Squared value</i>	69.7%	45.5%	69.7%	37.5%	60.5%	64.3%	52.6%	52.9%	31.2%	67.2%	45.5%

^aOnly one model applied, since TTHM was not statistically significant.

[Note: We kept in the model the variables which were statistically significant or, if not statistically significant, changed the R^2 – adjusted by 5%].

better relationships. On the other hand, it is believed that the models reflect the plots of water quality parameters and THAA reasonably well (Appendix 1, available online at <http://www.iwaponline.com/jws/060/047.pdf>).

SDS-HAA test result

The mean concentrations of individual HAA species by residence time found in field samples taken at the same time as the SDS study are shown in Table 6. The four compounds MCAA, MBAA, CDBAA and TBAA were not detected in any samples. Similar results were found in the SDS test (Table 7), and in both cases there was a general trend of increasing HAAs with residence time. The concentration of total HAA and individual species are comparable immediately after chlorination (i.e. 11.4 µg/l for TCAA in the field sample and 11.5 µg/l in the test, respectively). DCAA and TCAA were the two dominant HAAs species in both the field and test samples. Levels of total HAAs and residual chlorine from the water treatment works and the bench-top SDS test are compared in Figure 1. For the residual chlorine concentration, it can be seen that chlorine is consumed much

Table 6 | Occurrence of individual HAAs from the water supply system at the same time as SDS experiment (µg/l)

Residence time (h)	DCAA	TCAA	BCAA	BDCAA	DBAA
0	12.0	11.4	2.7	2.1	0.3
3	13.3	13.1	3.0	2.7	0.3
6.5	15.8	17.8	3.8	3.8	0.4
9	22.7	26.9	4.6	4.8	0.5

Table 7 | Occurrence of individual HAAs from the SDS test in laboratory (µg/l)

Residence time (h)	DCAA	TCAA	BCAA	BDCAA	DBAA
0	10.8	11.5	2.2	1.8	0.2
2	11.1	11.6	2.3	1.7	0.2
12	16.2	16.2	3.4	2.2	0.4
24	17.8	17.5	3.4	2.6	0.3
48	18.2	17.2	3.4	2.4	0.3
72	22.9	22.1	4.1	3.0	0.4
96	25.0	23.9	4.3	3.3	0.4
120	19.3	18.0	3.6	2.1	0.3
168	20.9	20.0	4.2	2.6	0.4

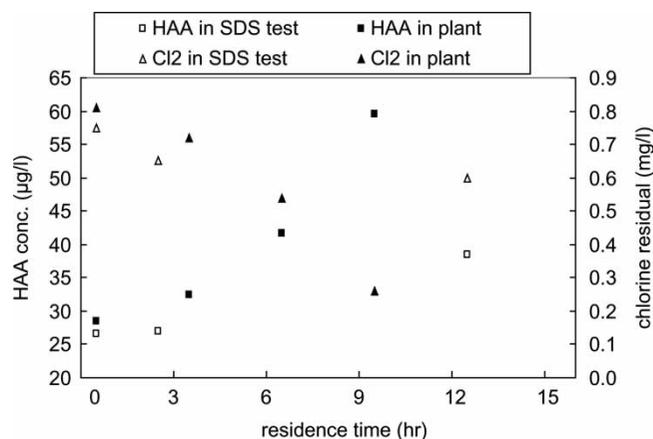


Figure 1 | Total HAA levels in the SDS test and field measurements by residence time.

faster in the distribution network than in the SDS test. A similar observation was reported by Rossman *et al.* (2001), where the rate of chlorine decay in the pipe was an order of magnitude greater than in the glass bottles. The concentrations of total HAAs yielded from the treatment plant were slightly higher than those from the SDS test, except at the point of water supply zone 3 (with a residence time of 9 h), which is almost 150% higher than the concentration from the SDS test. This may have been caused by a fast formation reaction in the system. As described previously, residual chlorine in the system reacts with various substances in the water and at the pipe walls resulting in the growth of HAAs. In this study, the residual chlorine was 0.26 mg/l at this point (with residence time of 9 h), while in the SDS test, the residual chlorine concentration was more than 0.6 mg/l. Because disinfection conditions vary from system to system, it is impossible to compare SDS DBPs in various systems or laboratories. Even in the same system, the variation of the water temperature from season to season could significantly limit the utility's ability to evaluate the DBP precursor removal efficiency. We also found that in the main study for the empirical modelling there was little evidence of an increase of HAAs with residence time (Table 8) suggesting that the SDS test may be fairly specific and sensitive to certain conditions. Notwithstanding these effects, an extensive study in the US using nationally collected data reported that the SDS method was a reasonably accurate method of predicting changes in HAA compound concentrations between the treatment plant and distribution system locations (AWWA 2002).

Table 8 | Occurrence of individual HAAs ($\mu\text{g/l}$) by residence time during the overall sampling period

Residence Time (h)	n^a	THAA	DCAA	TCAA	BCAA	BDCAA	DBAA
0	4	14.2	5.09	5.6	1.59	1.53	0.41
3–4	20	18.9	6.24	8.2	1.57	2.54	0.34
5.5–7	16	24.2	7.69	11.5	1.83	2.85	0.35
8–9	12	22.1	6.92	10.4	1.7	2.73	0.33
42–46	12	22.8	6.95	10.8	1.75	2.89	0.35

^aNumber of samples.

CONCLUSIONS

This is the first study to consider the predictors of HAAs in the UK. A statistical analysis has been carried out using measurements of HAA concentrations and other water quality parameters from a UK water supply system employed as a case study. The sampling showed that the total HAA concentration varied from 11.1 to 41.0 $\mu\text{g/l}$, and the dominant HAA species were trichloroacetic acid and dichloroacetic acid. The statistical predictive models explained between 31 and 70% of the variation in HAA levels, with models including THMs as predictors showing the highest explained variance (53–70%), and without THMs a lower variance (31–61%). Statistically significant predictors were THM levels, pH, temperature, total chlorine, total organic carbon, UV_{254} , bromine and residence time, but the importance of each varied with HAA species.

The use of the SDS-HAA test included both HAA concentration and speciation, and the concentration of total HAA and individual compounds were comparable after chlorination. With increasing of flow residence time, the concentrations of total HAAs in the water distribution system were higher than those found in the SDS test. A much faster rate of chlorine consumption was observed in the actual distribution system than in the SDS system. The difference between the results from the statistical predictive models and the SDS is that flow residence time showed an effect in the latter but not in the former. This may be partly due to some of the limitations of the statistical predictive methods, namely the need for many observations, only including one system, and the complexity of the system

and interaction of different parameters that makes it harder to model what is happening in the real world. Finally, other studies have used transformations of the HAA and water quality data when constructing statistical predictive models (see Table 1), which makes it harder to compare and interpret the models. In this study there was no need for undertaking such transformations, thereby making the models simpler and easier to interpret. The models also appeared to describe well what was observed in the plots with the raw data providing further confidence. However, at times the results were counterintuitive and these need to be further explored. It may be that the use of the model is limited to water systems with characteristics very similar to those observed here.

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