



Research note

Haloacetic acids and trihalomethanes in finished drinking waters from heterogeneous sources

C.M. Villanueva^{a,b,c,*}, M. Kogevinas^a, J.O. Grimalt^b^a *Respiratory and Environmental Health Research Unit, Municipal Institute of Medical Research (IMIM), CIDoctor Aiguader 80, 08003-Barcelona, Spain*^b *Department of Environmental Chemistry, Institute of Chemical and Environmental Research (CSIC), Jordi Girona 18, 08034-Barcelona, Spain*^c *Genetics and Microbiology Department, Universitat Autònoma de Barcelona (UAB), Campus de Bellaterra, 08193-Bellaterra, Spain*

Received 9 April 2001; received in revised form 13 February 2002; accepted 18 July 2002

Abstract

Trihalomethanes (THM) and haloacetic acids (HAA) are the most frequent chlorination by-products (CBP) in finished drinking waters. Traditionally, THM have been used as surrogates for CBP although the quantitative association between THM and other CBP is not well established. This problem is addressed in the present study from the analysis of THM and HAA in drinking water samples from four Spanish regions, representing areas with very different CBP composition, e.g. between 86 and 8.0 µg/l of THM and 50–3.0 µg/l of HAA.

The resulting dataset exhibit a statistically significant correlation between total THM and HAA (Pearson's correlation coefficient, $r_p = 0.815$, $p < 0.0005$). Furthermore, specific HAA are highly correlated with specific THM or their combinations. Accordingly, multivariate linear regression analysis of the concentrations observed show that the levels in total and specific HAA can be predicted from the THM content. These results are relevant for epidemiological studies on health effects from CBP exposure since they usually involve comparison of populations consuming waters of very distinct quality.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Drinking water; Chlorination by-products (CBP); Trihalomethanes (THM); Haloacetic acids (HAA); Bromide; Speciation**1. Introduction**

Since the first chlorination by-products (CBP) were detected in drinking waters early in the 1970s, several studies have evaluated their chemical properties, toxicology and human health effects [1]. Although epidemiological studies suggest that probable health effects of these compounds in humans may be related to cancer [2]

and birth defects [3], causal association is still undemonstrated [4].

Traditionally, trihalomethanes (THM) have been the most studied CBP and have been usually used as surrogates of these products. However, the association to other compounds such as haloacetic acids (HAA) has not been previously addressed in environmental epidemiology studies. Chlorinated drinking water contains a complex mixture of CBP with different chemical and toxicological properties that may eventually enter the human body by ingestion, inhalation and dermal absorption [5]. In this context, speciation of CBP deserves increasing attention, e.g. toxicological differences between brominated and chlorinated CBP (International Programme on Chemical Safety) [6].

*Corresponding author. Respiratory and Environmental Health Research Unit, Municipal Institute of Medical Research (IMIM), C/Doctor Aiguader 80, 08003-Barcelona, Spain. Tel.: +34-93-225-75-92; fax: +34-93-221-64-48.

E-mail address: cvillanueva@imim.es (C.M. Villanueva).

Chlorine is the drinking water disinfectant mostly used in Spain, a country with different climates and heterogeneous quality of water sources. Accordingly, four waters of diverse origins have been chosen to investigate the quantitative relationships between these compounds. These diverse compositions give rise to different levels and CBP composition in chlorinated drinking waters providing a good case for the study of the changes in THM and HAA levels in finished drinking waters from heterogeneous sources. The results are aimed to model HAA levels on the basis of THM levels, those more systematically determined in drinking waters, in order to provide more ground for the interpretation in epidemiology.

2. Materials and methods

2.1. Areas of study

Four provinces of Spain with different drinking water sources were selected for study: Barcelona, Alacant, Asturias and Tenerife (Fig. 1). Drinking water supplied in Barcelona, Alacant and Asturias mainly comes from surface sources. Drinking water supplied in the island of Tenerife (Canary Islands) originates from ground sources.

Eighty-eight drinking water samples were taken for the analysis of THM, 34 in Asturias, 25 in Barcelona, 19 in Alacant and 10 in Tenerife. HAA were analysed in a subset of 18 samples: five each in Barcelona, Asturias and Alacant and three in Tenerife.

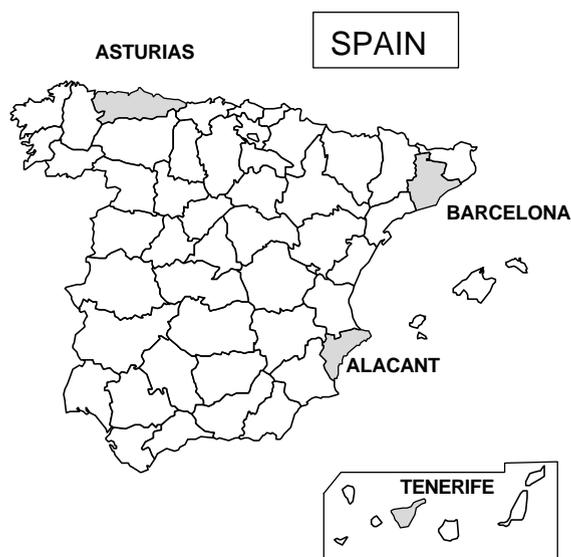


Fig. 1. Situation of the four sampling areas.

2.2. Sampling

For the analysis of THM, tap water samples were collected avoiding bubble formation and stored by duplicate in 40 ml glass vials. At sampling, 3 mg of sodium thiosulphate were added to each vial for quenching additional CBP formation. The vials were sealed with Teflon-faced rubber septums and open-top screw plugs. No air camera was left between the water and the screw plug.

For the analysis of HAA, water samples were taken in 250 ml glass bottles that were also sealed with Teflon-faced rubber screw plugs.

All samples were kept at 4°C until analysis, which was performed no later than 14 days after sampling.

2.3. Experimental analysis

Four THM (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were analysed following a previously optimised procedure [7]. Five millilitres of water was introduced into a purge and trap device and was bubbled with helium at a flow-rate of 40 ml/min for 11 min. The volatile compounds were retained in a tube packed with Tenax TA. These compounds were then analysed with a Perkin–Elmer Automatic Thermal Desorption Model 400 coupled to a Perkin–Elmer Autosystem gas chromatograph with an electron capture detector.

Nine HAA (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic, dibromoacetic, tribromoacetic, bromochloroacetic, dibromochloroacetic and dichlorobromoacetic acids) were analysed. The analytical procedure has been described in detail elsewhere [8]. Briefly, 30 ml water samples were treated with 2-bromopropionic acid, concentrated sulphuric acid, anhydrous sodium sulphate, copper (II) sulphate pentahydrate and methyl *tert*-butyl ether (MtBE). One micro litre of the MtBE extract was finally injected into a gas chromatograph equipped with electron capture detection.

2.4. Statistical analysis

Correlation between total THM and HAA was examined through simple linear regression analysis using an SPSS 9.0 package, introducing total THM level as the independent variable, and total HAA level as the dependent variable.

Multivariate linear regression analysis was used to elucidate which specific THM were the best predictors for the HAA compounds. For each single HAA the four THM were correlated as independent variables and those lacking statistical significance ($p > 0.05$) were excluded. Consecutive multiple linear regression models were performed and further THM were excluded if they were not significantly correlated to the HAA. The

procedure was repeated until the model only included statistically significant THM species.

3. Results and discussion

3.1. Raw water characteristics

Chloride content and organic carbon (measured as chemical oxygen demand) in the four sampling sites are reported in Table 1. As expected, the surface waters from the Mediterranean regions, Barcelona and Alacant are those exhibiting higher chloride and organic carbon, since they are reused several times for agricultural irrigation and they also receive urban and industrial effluent discharges. Ground waters in Tenerife exhibit higher chloride concentration than those in Asturias, which probably witness the intrusion of some proportion of saline water in the aquifer. The waters from this island are those with lower organic matter content, which is in agreement with the low pollution load expected for ground waters. The waters from Asturias exhibit the lowest chloride concentration of the series, which is consistent with the high amounts of rain collected by the river system in this region.

3.2. THM in finished drinking water

Total and specific THM levels are shown in Table 2. The Mediterranean area (Alacant and Barcelona) exhibits the highest levels (85.9 and 63.6 $\mu\text{g/l}$, respectively) while Tenerife exhibits the lowest (8 $\mu\text{g/l}$). Thus, total THM levels increase from low levels in ground waters (Tenerife) to low-intermediate levels in good-quality surface waters (Asturias) and high levels in poor-quality surface waters (Barcelona and Alacant).

THM speciation varies significantly among areas. The northern province (Asturias) presents the highest proportion of chloroform (60%) whereas both Mediterranean regions (Barcelona and Alacant) show a higher proportion of brominated and chloro-brominated species (70–80%). The island of Tenerife exhibits the highest proportion of brominated and chloro-

Table 1

Concentration of chloride and organic matter (measured as chemical oxygen demand, COD) in the raw waters from the areas selected for study

	Chloride (mg/l)	COD (mg O ₂ /l)
	Average (standard deviation)	
Alacant	360 (210)	17 (18)
Barcelona	280 (150)	5.1 (0.62)
Asturias	14 (6.8)	4.2 (4.0)
Tenerife	72 (55)	0.60 (0.11)

Table 2

Concentrations of trihalomethanes ($\mu\text{g/l}$) in the different areas of study

	Alacant	Barcelona	Asturias	Tenerife
Chloroform (CHCl ₃)				
Average	13.60 (5.33)	20.00 (10.56)	14.57 (7.14)	0.39 (0.21)
(s.d.)				
Min.	4.93	8.26	2.56	<0.1
Max.	24	35.25	29.54	0.68
Median	17.63	19.21	12.91	0.42
Bromodichloromethane (CHCl ₂ Br)				
Average	24.73 (5.07)	22.68 (5.46)	4.96 (2.59)	0.85 (0.67)
(s.d.)				
Min.	11.2	7.00	1.1	<0.5
Max.	30.8	31.46	12.43	1.95
Median	21.07	22.20	5.13	0.69
Dibromochloromethane (CHBr ₂ Cl)				
Average	25.67 (11.36)	10.81 (8.32)	2.23 (1.61)	1.18 (0.76)
(s.d.)				
Min.	6.55	2.86	0.07	0.5
Max.	40.99	36.10	6.7	3.2
Median	30.37	8.12	1.66	0.93
Bromoform (CHBr ₃)				
Average	21.93 (12.96)	10.19 (12.24)	0.56 (0.52)	5.55 (3.23)
(s.d.)				
Min.	4.5	0.02	0.05	2.8
Max.	44.28	40.10	1.84	11.8
Median	23.4	2.28	0.48	3.96
Total trihalomethanes				
Average	85.93 (30.62)	63.64 (20.57)	22.25 (5.54)	8.00 (3.44)
(s.d.)				
Min.	35.2	34.56	6.36	5.08
Max.	125.34	121.7	44.54	16.28
Median	69.23	55.59	22.34	7.07
<i>n</i>	19	25	34	10

brominated THM (> 90%). The levels of CBP are related to the amount of organic matter in the water samples [9]. Thus, the waters exhibiting higher CBP content (Table 2) are those with higher organic matter load (Table 1).

These results are consistent with those from a European survey conducted recently [10] that showed average THM levels of 78 $\mu\text{g/l}$ (standard deviation, s.d., 100, $n = 19$) and 7.6 $\mu\text{g/l}$ (s.d. 6.7, $n = 3$) for surface and ground waters, respectively.

THM speciation varies greatly according to water source.

3.3. HAA in finished drinking water

Total and specific HAA levels in the areas of study are shown in Table 3. Similarly to THM, the Mediterranean

Table 3
Concentrations of haloacetic acids ($\mu\text{g/l}$) in the areas of study

	Alacant	Barcelona	Asturias	Tenerife
Chloroacetic acid ($\text{ClCH}_2\text{CO}_2\text{H}$)				
Average (s.d.)	<0.3 (0)	0.87 (1.61)	<0.3 (0)	<0.3 (0)
Min.	<0.3	<0.3	<0.3	<0.3
Max.	<0.3	3.75	<0.3	<0.3
Median	<0.3	0.15	<0.3	<0.3
Dichloroacetic acid ($\text{Cl}_2\text{CHCO}_2\text{H}$)				
Average (s.d.)	12.03 (5.79)	7.10 (6.84)	4.29 (1.94)	0.25 (0.02)
Min.	6.75	0.62	1.74	0.24
Max.	21.45	15.44	6.24	0.27
Median	11.85	5.30	4.93	0.24
Trichloroacetic acid ($\text{Cl}_3\text{CCO}_2\text{H}$)				
Average (s.d.)	10.61 (8.39)	5.90 (4.82)	6.65 (1.64)	0.13 (0.03)
Min.	5.70	0.42	4.87	0.10
Max.	25.49	10.22	8.60	0.16
Median	7.25	8.52	7.26	0.13
Bromoacetic acid ($\text{BrCH}_2\text{CO}_2\text{H}$)				
Average (s.d.)	0.44 (0.56)	1.53 (1.31)	0.69 (0.36)	0.62 (0.14)
Min.	<0.1	0.51	<0.1	0.48
Max.	1.27	3.51	0.93	0.75
Median	0.05	0.82	0.83	0.62
Dibromoacetic acid ($\text{Br}_2\text{CHCO}_2\text{H}$)				
Average (s.d.)	5.16 (1.86)	6.49 (6.88)	0.40 (0.22)	1.31 (1.11)
Min.	2.40	0.39	<0.1	0.14
Max.	7.38	17.00	0.59	2.36
Median	5.72	5.22	0.50	1.42
Tribromoacetic acid ($\text{Br}_3\text{CCO}_2\text{H}$)				
Average (s.d.)	0.62 (0.70)	1.67 (1.93)	<0.1 (0)	0.35 (0.27)
Min.	<0.1	<0.1	<0.1	<0.1
Max.	1.74	3.812	<0.1	0.58
Median	0.45	0.72	<0.1	0.50
Bromochloroacetic acid ($\text{BrClCHCO}_2\text{H}$)				
Average (s.d.)	9.26 (5.33)	5.08 (3.80)	1.08 (0.41)	0.20 (0.04)
Min.	2.84	1.35	0.70	0.15
Max.	17.22	11.09	1.72	0.22
Median	9.38	5.12	1.03	0.22
Dibromochloroacetic acid ($\text{Br}_2\text{ClCCO}_2\text{H}$)				
Average (s.d.)	4.10 (1.61)	2.57 (2.04)	0.24 (0.27)	<0.1 (0)
Min.	2.01	0.90	<0.1	<0.1
Max.	6.00	5.77	0.54	<0.1
Median	4.47	1.72	0.05	<0.1

Table 3 (continued)

	Alacant	Barcelona	Asturias	Tenerife
Bromodichloroacetic acid ($\text{BrCl}_2\text{CCO}_2\text{H}$)				
Average (s.d.)	8.04 (4.00)	4.60 (3.65)	1.74 (0.16)	0.09 (0.04)
Min.	3.06	0.90	1.52	<0.1
Max.	14.06	9.45	1.94	0.12
Median	8.32	5.09	1.78	0.10
Total haloacetic acids				
Average (s.d.)	50.41 (22.35)	35.81 (19.41)	15.30 (1.32)	3.14 (1.41)
Min.	31.15	12.81	13.81	1.72
Max.	87.00	65.42	16.92	4.54
Median	46.03	34.61	14.92	3.71
<i>n</i>	5	5	5	3

coastal waters (Alacant and Barcelona) exhibit the highest HAA levels (50.4 and 35.8 $\mu\text{g/l}$, respectively) and Tenerife the lowest (3.1 $\mu\text{g/l}$). Mean HAA levels in European surface and ground waters are 9.25 (s.d. 7.7) and 0.83 $\mu\text{g/l}$ (s.d. 0.76), respectively [10]. Cancho et al. [8] described HAA levels in water from Barcelona in the order of 21.6 $\mu\text{g/l}$.

The highest proportion of chlorinated HAA is found in the Asturian waters (monochloroacetic, dichloroacetic and trichloroacetic acids > 60%) whereas both Mediterranean regions (Barcelona and Alacant) show a higher proportion of brominated and chloro-brominated species (50–60%). The waters from Tenerife exhibit the highest proportion of brominated and chloro-brominated HAA (> 80%).

Dichloroacetic acid is the most abundant compounds in the Mediterranean areas. Trichloroacetic and dibromoacetic acids are the second most abundant compounds in Alacant and Barcelona, respectively. The waters from Asturias contain trichloroacetic acid in highest abundance, dichloroacetic acid being the second. In Tenerife waters the most abundant compounds are brominated species, their composition being dominated by dibromoacetic and bromoacetic acids which rank as first and second main compounds, respectively.

Chloroacetic acid is the least common HAA in all areas, which is in agreement with analyses from other sites [11]. Tribromoacetic acid is the second less common.

3.4. THM–HAA correlations

The correlation between THM and HAA is based on the dataset in which HAA concentrations were available. The representativeness of this sub-sample for the whole dataset was checked by comparison of the average THM levels in both groups and no significant differences ($p < 0.05$) were found between them.

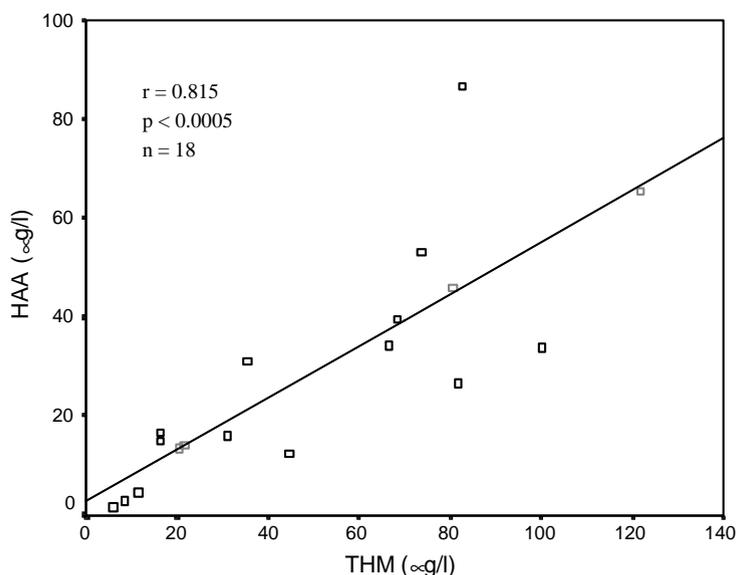


Fig. 2. Scatter plot showing the correlation between total THM and HAA levels.

Table 4
Models predicting the concentrations of specific HAA from those of THM

Haloacetic acids (Y_i)	Best predictor (X_i) ^a	Model ^a	Regression coefficient	Model statistical significance
Dibromochloroacetic	CHClBr_2	$Y_1 = -0.119 + 0.159X_3$	$r = 0.967$	$p < 0.0005$
Dichloroacetic	CHCl_2Br CHBr_3	$Y_2 = 1.534 + 0.566X_2 - 0.258X_4$	$r = 0.939$	$p < 0.0005$
Tribromoacetic	CHBr_3	$Y_3 = -0.13 + 0.0898X_4$	$r = 0.922$	$p < 0.0005$
Bromodichloroacetic	CHCl_3 CHClBr_2 CHBr_3	$Y_4 = -0.154 + 0.131X_1 + 0.277X_3 - 0.125X_4$	$r = 0.911$	$p < 0.0005$
Dibromoacetic	CHClBr_2 CHBr_3	$Y_5 = -0.046 + 0.143X_3 + 0.192X_4$	$r = 0.876$	$p < 0.0005$
Bromochloroacetic	CHClBr_2 CHBr_3	$Y_6 = 1.045 + 0.409X_3 - 0.212X_4$	$r = 0.844$	$p < 0.0005$
Monobromoacetic	CHBr_3	$Y_7 = 0.442 + 0.0459X_4$	$r = 0.680$	$p = 0.003$
Trichloroacetic	CHCl_3	$Y_8 = 1.269 + 0.375X_1$	$r = 0.658$	$p = 0.003$
Monochloroacetic	CHBr_3	$Y_9 = -0.028 + 0.0399X_4$	$r = 0.573$	$p = 0.016$

^a $X_1 = [\text{CHCl}_3]$, $X_2 = [\text{CHCl}_2\text{Br}]$, $X_3 = [\text{CHClBr}_2]$, $X_4 = [\text{CHBr}_3]$.

Linear regression analysis reveals a high and statistically significant correlation between total THM and total HAA, $Y = 2.643 + 0.526X$, Pearson's correlation coefficient ($r = 0.851$, $p < 0.0005$; $Y =$ total HAA ($\mu\text{g/l}$), $X =$ total THM ($\mu\text{g/l}$) (Fig. 2).

Multivariate linear regression analysis shows that some HAA are highly correlated to specific THM. The

concentrations of dibromochloroacetic, dichloroacetic, tribromoacetic, and bromodichloroacetic acids are highly correlated with those of some THM ($r > 0.9$, $p < 0.0005$, Table 4). Thus variation of some THM may explain $> 81\%$ of the variability of these four HAA. Dibromoacetic and chlorobromoacetic acids are also correlated with THM but with a lower correlation

coefficient ($r > 0.8$, $p < 0.0005$). Chloroacetic, trichloroacetic and bromoacetic acids are less correlated with THM ($r = 0.573, 0.658$ and 0.680 respectively).

The more brominated THM (bromoform and dibromochloromethane) are those with highest predictive capacity, fully or partially, explaining the concentrations of eight of the nine HAA examined. Chloroform is only correlated to trichloroacetic acid and bromodichloromethane to dichloroacetic acid (in part). Surprisingly, the only THM that correlates significantly with monochloroacetic acid is bromoform.

4. Conclusions

- Total THM and HAA vary considerably between different drinking waters according to their water sources. Low CBP levels are observed in ground waters, low-intermediate levels in good-quality surface waters and high levels in poor-quality surface waters. THM and HAA speciation also varies substantially among different water sources.
- Despite these differences, total and specific HAA species show a high correlation with total and specific THM compounds. Thus, HAA levels could be predicted from THM concentrations.
- The linear regression equations calculated from these correlations may be useful for the estimation of HAA concentrations from THM. This approach may find applicability in environmental and toxicological studies for assessment of human health risk of chlorinated by-products in drinking water.

Acknowledgements

We thank Esther Marco for her assistance in the laboratory, and the EPICURO team for their collaboration taking the water samples. We are grateful to AGBAR and Dr. Ventura for some of the analyses. This project is partially funded by the CIRIT Grant No. 1999SGR 00241 and the FIS Grants 98/1274 and 01/

1326. CMV thanks CIRIT (Generalitat de Catalunya) for a Ph.D. fellowship.

References

- [1] World Health Organisation (WHO). Guidelines for drinking-water quality, 2. Health criteria and other supporting information. Geneva: World Health Organisation, 1996.
- [2] Cantor KP. Drinking water and cancer. *Cancer Causes and Control* 1997;8(3):292–308.
- [3] Nieuwenhuijsen MJ, Toledano MB, Eaton N, Fawell J, Elliott P. Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. *Occup Environ Med* 2000;57(2):73–85.
- [4] International Agency for Research on Cancer (IARC). Chlorinated drinking water, chlorination by products, some other halogenated compounds, cobalt and cobalt compounds, vol 52. Lyon: IARC, 1991.
- [5] Weisel CP, Jo WK. Ingestion, inhalation, and dermal exposures to chloroform and trichloroethene from tap water. *Environ Health Perspect* 1996;104(1):48–51.
- [6] International Programme on chemical safety (IPCS). Disinfectant and disinfectant by-products. Environmental Health Criteria 216, United Nations Environment Programme (UNEP), International Labour Organization (ILO), World Health Organization (WHO), Geneva, 2000.
- [7] Amaral OC. Analysis and behaviour of organohalogenated compounds in water, air and sediments from rural, urban and industrial zones. Ph.D. thesis, University of Barcelona, 1994.
- [8] Cancho B, Ventura F, Galceran MT. Behavior of halogenated disinfection by-products in the water treatment plant of Barcelona, Spain. *Bull Environ Contam Toxicol* 1999;63(5):610–7.
- [9] 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(12):2635–42.
- [10] Palacios M, Pampillón JF, Rodríguez ME. Organohalogenated compounds levels in chlorinated drinking waters and current compliance with quality standards throughout the European union. *Water Res* 2000;34(3):1002–16.
- [11] Pourmoghaddas H, Stevens AA, Kinman RN, Dressman RC, Moore LA, Ireland JC. Effect of bromide ion on formation of HAAs during chlorination. *J Am Water Works Assoc* 1993;85(1):82–7.