Environ Monit Assess (2010) 162:237–250
DOI 10.1007/s10661-009-0792-1

Occurrence of haloacetic acids (HAAs) and trihalomethanes (THMs) in drinking water of Taiwan

H. H. Chang · H. H. Tung ·
C. C. Chao · G. S. Wang

Received: 22 August 2008 / Accepted: 27 January 2009 / Published online: 7 March 2009

Abstract In this study, water samples were collected from 86 water treatment plants for analysis of haloacetic acids (HAAs) and trihalomethanes (THMs) from February to March, 2007 and from July to August, 2007. Both seasonal and geographical variations of disinfection by-products (DBPs) in drinking water of Taiwan were presented. The results showed that the five HAA concentrations (HAA5) were 1.0–38.9 μg/L in the winter and 0.2–46.7 μg/L in the summer; and the total THMs were ND-99.4 μg/L in the winter and ND-133.2 μg/L in the summer. For samples taken from the main Taiwan island, dichloroacetic acid (29.4–31.7%) and trichloroacetic acid (25.3–27.6%) were the two major HAA species, and trichloromethane was the major THM species (49.9–62.2%) in finished water. For water treatment plants located on the offshore islands outside of Taiwan, high bromide concentration was found in raw water, and higher percentage of brominated THMs and HAAs were formed in the overall formation. A statistically significant ($P < 0.005$) logarithmic linear regression model was found to be useful to describe the correlations between TTHM and HAA5 or nine HAAs ($\text{HAA5} = 1.219 \times \text{TTHM}^{0.754}$, $R^2 = 0.658$; $\text{HAA9} = 1.824 \times \text{TTHM}^{0.735}$, $R^2 = 0.678$). No apparent difference was observed for DBPs concentrations between finished water and distribution samples in this study.

Keywords Trihalomethanes · Haloacetic acids · Drinking water · Disinfection by-products

Introduction

Due to its high oxidizing potential and the residual disinfection ability in the distribution systems (Elshorbagy et al. 2000), chlorine is widely used in Taiwan as a primary disinfectant. Since the first category of halogenated disinfection by-products (DBPs), THMs, were detected in drinking water in the early 1970s (Rook 1974), more than 250 different classifications of DBPs were identified including haloacetic acids (HAAs), haloaldehydes, haloketones, nitrosamines, etc. Although many studies have found potentially more toxic DBPs, such as nitrogenous DBPs, THMs and HAAs are

H. H. Chang · G. S. Wang (✉)
Institute of Environmental Health,
College of Public Health, National Taiwan University,
Taipei, Taiwan, Republic of China
e-mail: gswang@ntu.edu.tw

H. H. Tung · C. C. Chao
Institute of Environmental Engineering,
College of Engineering, National Taiwan University,
Taipei, Taiwan, Republic of China

still particularly concerned, since they are good indicators of the overall DBPs in chlorinated water (Sadiq and Rodriguez 2004; Krasner et al. 2006; Xie et al. 2006),

THMs include four species (TTHM): chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). Epidemiological studies showed that the chloroform in drinking water had a strong positive correlation with bladder cancer mortality rate, and the brominated-THM levels were related to the mortality rate of brain cancer (Cantor et al. 1978). Many investigations also demonstrated that THMs expressed various reproductive health effects for humans (Kramer et al. 1992; Bove et al. 1995; Waller et al. 1998). Therefore, THMs were classified as possible or probable human carcinogens and regulated by many environmental protection agencies worldwide.

The nine common HAA compounds (HAA9) include bromoacetic acid ($BrCH_2COOH$, MB AA), chloroacetic acid ($ClCH_2COOH$, MCAA), dibromoacetic acid ($Br_2CHCOOH$, DBAA), dichloroacetic acid ($Cl_2CHCOOH$, DCAA), bromochloroacetic acid ($BrClCHCOOH$, BCAA), tribromoacetic acid (Br_3CCOOH, TBAA), trichloroacetic acid (Cl_3CCOOH, TCAA), dibromochloroacetic acid ($Br_2ClCCOOH$, DBCAA), and bromodichloroacetic acid ($BrCl_2CCOOH$, BDCAA). These are nonvolatile (boiling points = 189–250°C), highly hydrophilic, and ionic compounds ($pKa = 0.55$–2.86; Urbansky 2000). Some studies showed that HAAs are more carcinogenic than THMs. DCAA was hepatoxic which promoted the cells accumulating the liver glycogen in rodents (Kato-Weinstein et al. 1998) and produced neurotoxicity (Stacpoole 1989). Maternal rat fed with 2,730 ppm of TCAA in drinking water demonstrated a significant increase in cardiac defects of fetus (Johnson et al. 1998). Both DCAA and DBAA showed adverse male reproductive effects in animal studies (Cicmanec et al. 1991; Toth et al. 1992; Linder et al. 1994). Some brominated-HAAs could induce oxidative damages to DNA in the liver (Parrish et al. 1996), or they were toxic for cecal microbiota and mutagenic in the microsuspension assay (Nelson et al. 2001). In some investigations, brominated-HAAs had slightly or more significantly adverse health effects than chlorinated-HAAs (Austin et al. 1996; Parrish et al. 1996; Giller et al. 1997).

In response to the potential human health concerns of DBPs, many countries or international organizations have promulgated regulations to control THMs and HAAs in drinking water. United States Environmental Protection Agency (USEPA) established the stage 1 Disinfectants/Disinfection By-Products Rule (D/DBPR) in December 1998. Besides promulgating the maximum contaminant level (MCL) of 80 μg/L for TTHM in the stage 1 D/DBPR, USEPA also regulated that the sum of five HAAs (MCAA, MBAA, DCAA, DBAA, and TCAA) should not exceed the MCL of 60 μg/L based on a running annual average (USEPA 1999b, 2001a). For protection of public health, World Health Organization (WHO) set the guidelines of MCAA, DCAA, and TCAA at 20, 50, and 200 μg/L (WHO 1993), respectively.

In Taiwan, sodium hypochlorite (NaOCl) and chlorine gas are the most widely used primary disinfectants in water treatments, and HAAs and THMs are the most abundant DBPs (by weight) in drinking water. The MCL for TTHM was regulated at 100 μg/L from 1998 by Taiwan Environmental Protection Agency and was reduced to 80 μg/L in 2006. Currently, no national standard for HAAs in drinking water was established in Taiwan. Some studies showed that the total nine HAA (HAA9) concentrations in drinking water could be as high as 118.0 μg/L and 103.1 μg/L in the southern part of Taiwan or in offshore islands during summer season (Chang 2004). However, it could be as low as not detectable in the northern part of Taiwan where better source water quality could be found (Chiang and Chang 2003).

Due to the lack of nationwide and long-term monitoring data to describe the profile of DBPs in Taiwan, it is important to establish a DBPs database for future water quality management purpose. The first objective of this study was to investigate a detailed seasonal and geographical DBPs distribution (include THMs and HAAs) in Taiwan. The second objective was to explore the species distribution of brominated and chlorinated DBPs. The third objective was to assess the correlation between HAAs and THMs by logarithmic linear regressions.

Materials and methods

Reagents

The THM standards containing the four trihalomethane (TCM, BDCM, DBCM, and TBM) and benzene-d6 (1,000 μg/mL each in methanol, purity >97.5%) were purchased from Supelco (Bellefonte, PA, USA). Separated standard solutions for HAAs analysis (1,000 μg/mL each in methyl tertiary butyl ether, MTBE; purity >96.2%), including MCAA, MBAA, DCAA, DBAA, BCAA, TCAA, TBAA, BDCAA, CD BAA, 1,2,3-trichloropropane (internal standard) and 2-bromobutanoic acid (surrogate standard), were also purchased from Supelco.

Field sampling program and sample collection

The raw water, finished water, and distribution samples of 86 water treatment plants (WTPs) in Taiwan were collected from February to March, 2007 (winter samples) and from July to August, 2007 (summer samples). The pH, water temperature, and free chlorine residuals were measured on site. The concentrations of THMs and HAAs for finished water and distribution samples were measured within 14 days after sampling. In addition, the nonpurgeable organic carbon (NPDOC) and UV absorbance at 254 nm (UV_{254}) of raw water were also analyzed. The $SUVA_{254}$ values were calculated by taking the UV_{254} values divided by the NPDOC values.

After water sampling, samples for NPDOC, UV_{254}, THMs, and HAAs measurements were kept in 4°C and shipped to the laboratory immediately. For THMs and HAAs analysis, chlorine-quenching agents (L-ascorbic acid and ammonium chloride, respectively) were added to the sample bottles onsite to avoid additional DBPs formation during the sample collection and shipping. All samples were refrigerated at 4°C until analysis or extraction.

Analytical methods

NPDOC was measured with an ASI 5000 TOC analyzer (Shimadzu, Tokyo, Japan). A UV 160A UV/Visible spectrophotometer (Shimadzu, Tokyo, Japan) was used for measuring the UV_{254}. All samples for NPDOC and UV_{254} were filtered by a 0.45-μm filter before measurement. Samples for THMs analysis were performed by purge and trap (Model 4660, OI Analytical, Texas, USA) and a gas chromatography with mass detector (Agilent 6890GC/5973MSD) equipped with a capillary column (RTX-VOC, 60 m × 0.32 mm inside diameter, 1.5 μm film thickness). The method detection limits (MDLs) of TCM, BDCM, DBCM, TBM were 0.16, 0.18, 0.14, 0.12 μg/L, respectively. HAA concentrations were determined according to the USEPA method 552.3 (USEPA 2003). Briefly, 40 mL of water samples were spiked with surrogate standard (20 μg/mL) and proceeded by liquid–liquid extraction using MTBE (4 mL) with 1,2,3-trichloropropane as the internal standard (1 μg/mL). The extracted HAA (3 mL) was methylated with 10% sulfuric acid in methanol (3 mL) at 50°C for 2 h. Two back extractions with sodium sulfate solution (150 g/L) and saturated sodium bicarbonate solution (7 mL) were followed after methylation. The HAA concentrations were determined by a gas chromatograph with electron capture detector (Agilent 6890GC/micro ECD), with DB-1701 column (30 m × 0.25 mm inside diameter, 0.25 μm film thickness). The method blanks, duplicate samples, and matrix spiked samples were examined to monitor the laboratory performance and data quality in each batch HAA extraction/analysis. The MDLs of MCAA, MBAA, DCAA, TCAA, BCAA, BDCAA, DBAA, CDBAA, and TBAA were 0.17, 0.10, 0.12, 0.08, 0.09, 0.06, 0.07, 0.05, and 0.10 μg/L, respectively.

Results and discussions

Raw water quality parameters

As shown in Fig. 1, the 86 WTPs were divided into five zones based on the geographic locations—northern, central, southern, eastern, and offshore islands. In winter, the NPDOC of raw water samples demonstrated the geographic distribution pattern: southern (5.5 ± 1.7 mg/L) > offshore islands (4.5 ± 1.1 mg/L) > central (3.9±2.1 mg/L) >

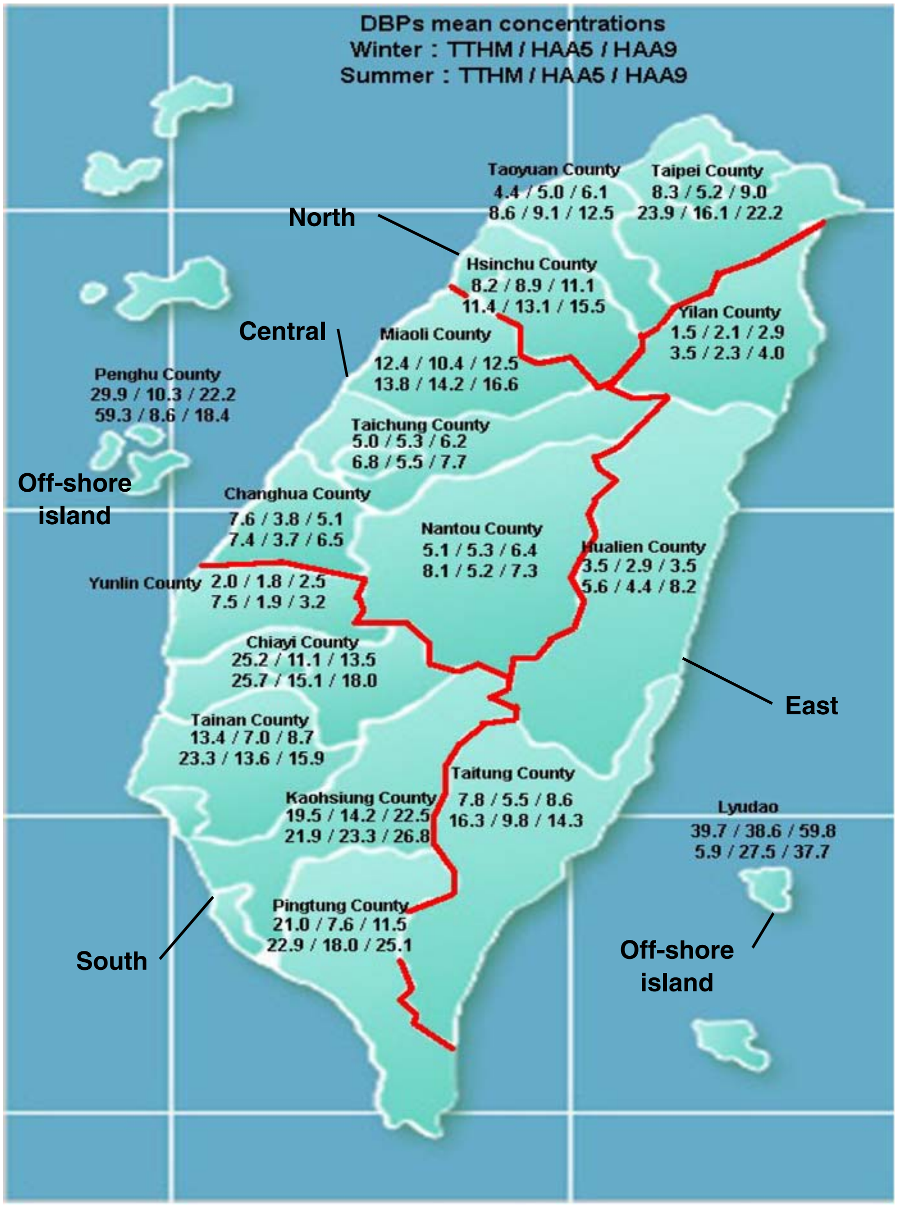

Fig. 1 Geographic distribution of mean DBPs concentrations in Taiwan

northern (1.6 ± 0.9 mg/L) > eastern (1.2 ± 0.5 mg/L) (Table 1). In summer, the highest mean NPDOC level (8.6 ± 11.3 mg/L) occurred in the offshore island region following by the southern region (1.9 ± 1.6 mg/L). The mean NPDOC levels of the other areas only showed a minor difference and were ranged between 1.2 and 1.5 mg/L. Due to water shortages, the offshore island region has poor raw water quality for a long time. For WTPs in the southern part of Taiwan, severe industrial and animal farming pollutions were ongoing regularly. With these constraints, the offshore islands and southern zones have showed relatively high NPDOC levels in raw water during different seasons. During this study, however, the relative low mean NPDOC concentrations of southern zone in summer were attributed to the heavy rainfalls around the sampling time. The eastern region has better source water quality, since it is less developed and has little industrial pollution.

Table 1 Distributions of water quality parameters and DBPs

		Winter (February–March, 2007)		Summer (July–August, 2007)	
		Mean ± SD	(Median, min, max)	Mean ± SD	(Median, min, max)
Northern WTPs ($n = 26$)	NPDOC[a] (mg/L)	1.6 ± 0.9	(1.4, 0.5, 3.5)	1.5 ± 0.5	(1.4, 0.4, 2.5)
	UV^{a}_{254} (cm^{-1})	0.020 ± 0.007	(0.020, 0.011, 0.040)	0.021 ± 0.009	(0.019, 0.007, 0.044)
	$SUVA^{a}_{254}$ (L mg^{-1}cm^{-1})	1.6 ± 0.9	(1.2, 0.6, 3.8)	1.4 ± 0.4	(1.5, 0.9, 2.5)
	TTHM (μg/L)	7.4 ± 4.5	(6.4, ND[b], 17.9)	16.0 ± 13.1	(12.6, ND, 62.9)
	HAA5 (μg/L)	6.3 ± 3.3	(5.3, 2.1, 15.1)	13.2 ± 8.7	(10.9, 2.1, 37.0)
	HAA9 (μg/L)	8.8 ± 3.8	(8.0, 3.7, 18.0)	17.5 ± 11.1	(15.0, 2.4, 48.8)
Central WTPs ($n = 22$)	NPDOC (mg/L)	3.9 ± 2.1	(2.8, 2.0, 8.4)	1.2 ± 0.4	(1.3, 0.5, 1.8)
	UV_{254} (cm^{-1})	0.023 ± 0.008	(0.022, 0.012, 0.043)	0.012 ± 0.009	(0.008, 0.002, 0.038)
	$SUVA_{254}$ (L mg^{-1}cm^{-1})	0.6 ± 0.2	(0.7, 0.3, 0.9)	1.0 ± 0.6	(0.7, 0.3, 2.7)
	TTHM (μg/L)	6.0 ± 5.5	(4.0, ND, 27.3)	7.5 ± 6.6	(5.2, 2.3, 30.3)
	HAA5 (μg/L)	4.8 ± 3.5	(3.5, 1.0, 13.8)	4.7 ± 3.2	(3.7, 0.9, 14.3)
	HAA9 (μg/L)	5.9 ± 3.8	(4.7, 1.6, 15.0)	7.1 ± 3.8	(6.1, 0.9, 17.3)
Southern WTPs ($n = 17$)	NPDOC (mg/L)	5.5 ± 1.7	(5.8, 2.9, 8.5)	1.9 ± 1.6	(1.6, 0.6, 7.0)
	UV_{254} (cm^{-1})	0.031 ± 0.020	(0.027, 0.010, 0.090)	0.022 ± 0.011	(0.026, 0.005, 0.043)
	$SUVA_{254}$ (L mg^{-1}cm^{-1})	0.6 ± 0.4	(0.5, 0.2, 1.4)	1.5 ± 0.8	(1.2, 0.2, 2.8)
	TTHM (μg/L)	19.8 ± 13.4	(19.7, 2.0, 62.1)	22.9 ± 13.3	(22.8, 4.8, 55.3)
	HAA5 (μg/L)	10.5 ± 7.6	(8.9, 1.6, 31.3)	16.7 ± 12.5	(13.2, 1.8, 46.7)
	HAA9 (μg/L)	14.5 ± 13.0	(10.4, 2.2, 61.8)	19.8 ± 14.2	(15.8, 3.2, 57.8)
Eastern WTPs ($n = 16$)	NPDOC (mg/L)	1.2 ± 0.5	(1.2, 0.5, 2.2)	1.3 ± 0.8	(1.2, 0.7, 3.4)
	UV_{254} (cm^{-1})	0.024 ± 0.019	(0.018, 0.011, 0.090)	0.013 ± 0.016	(0.009, 0.001, 0.065)
	$SUVA_{254}$ (L mg^{-1}cm^{-1})	2.2 ± 1.3	(1.7, 0.8, 5.0)	0.9 ± 0.5	(0.8, 0.1, 2.3)
	TTHM (μg/L)	4.9 ± 6.8	(3.0, ND, 25.2)	9.3 ± 10.6	(4.8, 2.1, 38.0)
	HAA5 (μg/L)	3.8 ± 3.6	(2.2, 1.2, 16.5)	6.2 ± 5.9	(4.4, 0.2, 26.9)
	HAA9 (μg/L)	5.3 ± 5.6	(3.1, 1.6, 23.7)	9.9 ± 8.2	(8.4, 0.2, 36.8)
Offshore island WTPs ($n = 5$)	NPDOC (mg/L)	4.5 ± 1.1	(4.7, 3.1, 6.0)	8.6 ± 11.3	(5.5, 1.0, 28.5)
	UV_{254} (cm^{-1})	0.066 ± 0.039	(0.075, 0.025, 0.111)	0.088 ± 0.082	(0.081, 0.003, 0.200)
	$SUVA_{254}$ (L mg^{-1}cm^{-1})	1.6 ± 1.2	(1.5, 0.5, 3.6)	1.3 ± 1.3	(1.0, 0.3, 3.6)
	TTHM (μg/L)	31.9 ± 29.8	(24.4, 5.6, 99.4)	48.6 ± 56.6	(6.7, 4.3, 133.2)
	HAA5 (μg/L)	16.0 ± 14.2	(7.1, 3.5, 38.9)	12.4 ± 10.3	(11.4, 1.9, 28.1)
	HAA9 (μg/L)	29.8 ± 23.2	(13.0, 10.3, 60.6)	22.2 ± 15.3	(19.9, 5.7, 41.2)

There was no statistical significance of THM and HAA concentrations between finished water and distribution samples (data not shown)

[a] NPDOC, UV_{254}, $SUVA_{254}$ were measured from raw water. TTHM and HAA5 were detected from finished water and distribution water

[b] *ND* not detected

UV_{254} is used as a surrogate of chromophores in natural organic matter (NOM). It has been shown that many kinds of chromophores were the precursors of DBPs. The results in Table 1 indicated that higher UV_{254} was observed in offshore island area, which could reach 0.066 ± 0.039 and 0.088 ± 0.082 cm^{-1} in winter and summer, respectively. For southern area, it was 0.031 ± 0.020 cm^{-1} in winter and 0.022 ± 0.011 cm^{-1} in summer. The other three areas had similar mean UV_{254} values in winter (0.020 ± 0.007 cm^{-1} for northern WTPs, 0.023 ± 0.008 cm^{-1} for central WTPs, and 0.024 ± 0.019 cm^{-1} for eastern WTPs). However, there was a slight difference in mean UV_{254} for northern (0.021 ± 0.009 cm^{-1}), central (0.012 ± 0.009 cm^{-1}), and eastern (0.013 ± 0.016 cm^{-1}) WTPs during summer, and these values were all lower than those observed in winter.

The characteristics of $SUVA_{254}$ distribution in Taiwan were not similar to the NPDOC distribution obtained in this study. A mean value of 2.2 ± 1.3 L mg^{-1}cm^{-1} was observed for the eastern region, which was the highest level in winter. After that 1.6 ± 1.2 L mg^{-1}cm^{-1}of offshore island region and 1.6 ± 0.9 L mg^{-1}cm^{-1} of northern region were the seconds. On the contrary, 0.6 ±

0.4 L $mg^{-1}cm^{-1}$ for southern WTPs and 0.6 ± 0.2 L $mg^{-1}cm^{-1}$ for central WTPs were the lowest levels. During the summer season, however, the southern WTPs showed the highest mean $SUVA_{254}$ (1.5 ± 0.8 L $mg^{-1}cm^{-1}$); followed with the northern (1.4 ± 0.4 L $mg^{-1}cm^{-1}$) and offshore island region (1.3 ± 1.3 L $mg^{-1}cm^{-1}$). The patterns of spatial distributions for $SUVA_{254}$ showed a large difference between winter and summer.

Distributions of HAAs and THMs

1. Average DBP concentrations

Table 1 shows the mean THMs and HAAs in different regions of Taiwan. The THMs levels in drinking water expressed a similar dispersive characteristic as NPDOC distribution. The highest mean THMs levels (31.9 ± 29.8 and 48.6 ± 56.6 μg/L for winter and summer, respectively) were obtained in offshore island area because of high NPDOC in raw water due to the long retention time in reservoirs. The second highest mean THMs (19.8 ± 13.4 and 22.9 ± 13.3 μg/L for winter and summer, respectively) occurred in southern Taiwan where the raw water was polluted by the domestic and agricultural wastewaters. The THMs in drinking water of central WTPs and eastern WTPs were the lowest.

As for the HAAs in drinking water in winter season, the offshore island WTPs also gave the highest mean HAA5 level (16.0 ± 14.2 μg/L), and the WTPs in other areas contained much lower HAA5 (most of them <10.5 μg/L). For summer season, the highest mean HAA5 (16.7 ± 12.5 μg/L) appeared in the southern region, and the order of HAA5 in the other regions was northern (13.2 ± 8.7 μg/L) > offshore islands (12.4 ± 10.3 μg/L) > eastern (6.2 ± 5.9 μg/L) > central (4.7 ± 3.2 μg/L). However, the highest mean HAA9 concentration still occurred in the offshore island's WTPs if brominated HAAs were counted. The difference between HAA5 and HAA9 levels suggested that the four brominated HAAs (BCAA, CDBAA, BDCAA and TBAA) should be considered in areas with relatively higher Br^- level in source waters. Overall, the mean DBP concentrations in summer were higher than in winter except for HAA5 and HAA9 in the offshore island WTPs. According to the investigation on WTPs in Quebec City (Rodriguez et al. 2007a, b), specific HAA decreased dramatically during filtration especially for DCAA. Degradation of DCAA in summer was probably due to conditions which were highly favorable for developing microbial activity within the filter. For the HAA concentrations observed in this study, it was possible that some HAAs would be degraded by the microbial activity in the offshore island WTPs. The relatively higher levels of HAA5 or HAA9 in winter also supported this observation, since lower microbial activity could be found in winter seasons.

2. Association between DBPs, NPDOC, and SUVA values

There was no consistent pattern between $SUVA_{254}$ and DBPs concentration (described later). Weishaar et al. (2003) suggested that $SUVA_{254}$ was strongly correlated with some aromatic organic matter (percent aromaticity, $R^2 = 0.97$) isolated from a different aquatic environment and could be a useful parameter for aromatic DOC. However, $SUVA_{254}$ had poor correlation with THM formation because certain aromatic molecules with contribution to UV_{254} would be inert to react with disinfectants to form THM, and some THM precursors did not contribute to the overall UV_{254}. Consequently, $SUVA_{254}$ also described the weak correlation with DBP concentration, and Weishaar et al. considered that it could not be a good predictor in the investigation. In this study, the result described later also showed a poor correlation between $SUVA_{254}$ and DBPs formation.

3. Geographic distribution

Figure 1 showed the geographic variations of mean DBP concentrations in different areas. The difference between HAA5 and HAA9 showed that HAA5 usually underestimated the overall HAA concentrations as well as the potential health risk that resulted from HAA exposure in drinking water.

The highest mean HAA5 (38.6 μg/L in winter) or THMs (59.3 μg/L in summer) occurred in the drinking water of offshore island region. In the offshore island area, that has the limited water resources and gains the source water only through rainfall stored in the reservoirs. In this situation, the longer retention time for the source water resulted in relatively higher NPDOC in raw water. In addition, the urban runoff releases the organic contaminants into the water consistently, even after the installation of the sanitary sewers. The algal bloom usually takes place in April or May due to severe eutrophication status. Finally, the seawater intrusion increases the levels of bromide in raw water (up to 0.8 mg/L), which leads to the formation of brominated DBPs and has replaced the chlorinated DBPs to be the major DBP species in the offshore island region.

In the southern area, the high HAAs or THMs levels were due to the uses of contaminated surface water as the raw water. The major rivers in southern Taiwan are mostly classified as heavily or moderately polluted rivers in 2007 (TWEPA 2007). In 2006, five out of the eight eutrophicated reservoirs (among the 21 monitored reservoirs) were located in this area. Moreover, the rate of public sewage systems in Kaohsiung City, the largest city in southern Taiwan, is only 45.1%. Under this condition, fairly high NOM in source water resulted in high DBPs in finished water after chlorination. The mean TTHM and HAA5 concentrations of southern WTPs could reach 22.9 ± 13.3 and 16.7 ± 12.5 in summer, respectively (Table 1). The highest value (23.3 μg/L) of HAA5 in Taiwan was observed in southern region (except the offshore island region) during summer season. However, very low levels of DBPs were also observed in southern Taiwan because of the installation of the advanced water treatment facilities including ozonation, granular activated carbon (GAC), and nanofiltration (NF) in some WTPs in Kaohsiung City. The mixed finished water from both traditional and advanced treatment process resulted in a dilution effect for DBPs levels to decrease the mean concentrations and result in large variations of DBP levels in those WTPs. On the other hand, many aquacultures located in the southern coast of Taiwan have extensive groundwater extractions that resulted in land subsidence. The bromide ion in the raw water due to seawater intrusion also resulted in the difference between HAA5 and HAA9. The proportion including BCAA and the other three brominated trihaloacetic acids was larger (7.1 μg/L in Pingtung) in southern Taiwan than in the other areas except the offshore island region.

Most rivers of the eastern region are unpolluted compared to the offshore islands or southern regions. The good source water quality led to the low THMs and HAAs in eastern Taiwan. The lowest mean DBP concentrations were in Yilan county (THM = 1.5–3.5 μg/L; HAA5 = 2.1–2.3 μg/L) and Hualien county (THM = 3.5–5.6 μg/L; HAA5 = 2.9–4.4 μg/L), consequently.

4. DBPs species distribution

In the main island, TCM was the major THM species which accounts for 49.9% and 62.2% of the total THMs in winter and in summer, respectively (Fig. 2a). BDCM was also a major THM species and had a higher proportion in winter (26.6%) than in summer (21.0%). Among the four THM species, TBM concentration was the lowest in Taiwan's finished water except for those offshore island WTPs (6.5%). In the offshore island area, BDCM was the most important THM species and accounted for 44.1% of total THMs in winter; however, DBCM was the most abundant THM in summer (41.1%). Compared with samples taken from other areas, TCM was the least common THMs in offshore island region and only accounted for approximately 13% in total THMs in finished water.

Figure 2b showed the species variations and the percentages of each HAA in different seasons and locations. There was no significant difference in species distribution between winter and summer, and the seasonal variation of species distribution was not apparent for HAAs. DCAA (29.4–31.7%) and TCAA (25.3–27.6%) were the two major HAA species found in Taiwan's drinking water except those in the offshore island region. BCAA was the next abundant compound (11.0–15.9%), and TBAA was the least common species except in the island region (<3%). In the offshore island region, DCAA was still the most abundant HAA (17.8–25.7%) due to the extensive uses of chlorine for controlling organic and inorganic pollutants in raw water. However, the second common HAA species observed in finished water was DBAA (18.4–20.0%) as a result of the higher bromide concentration in the raw

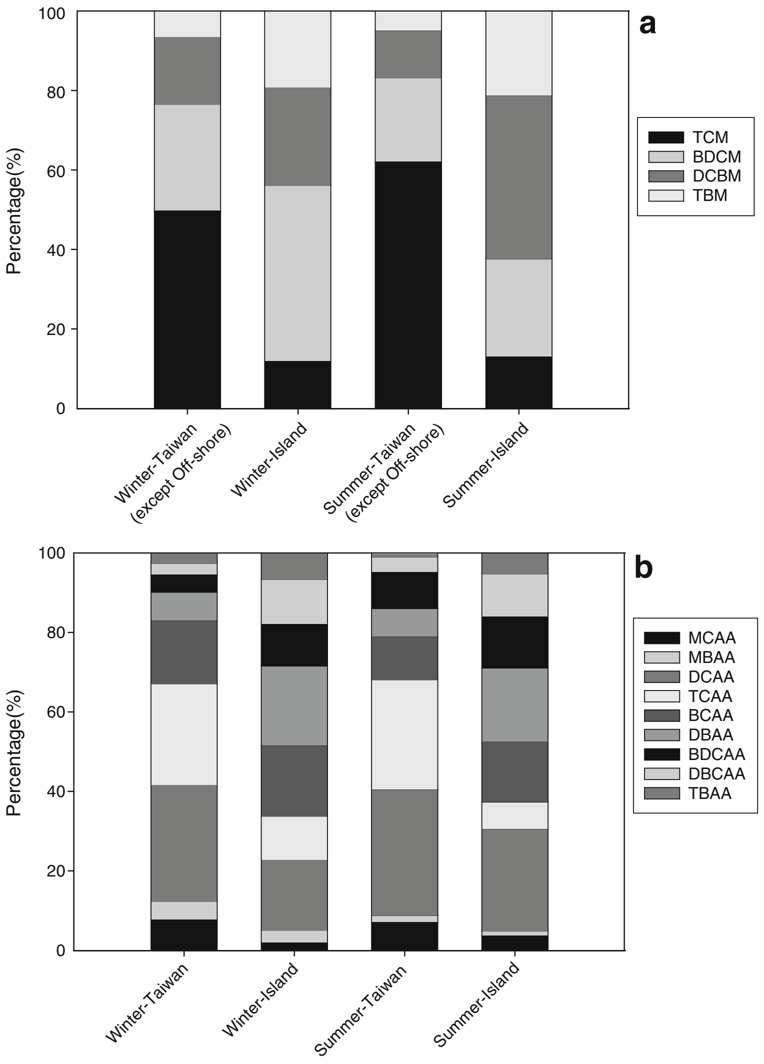

Fig. 2 Seasonal and regional THM (**a**) and HAA (**b**) species distributions

water. The portion of the total brominated tri-HAA (summation of BDCAA, DBCAA, and TBAA) ranged from 10% to 14% of total HAAs in Taiwan area, but it increased to 26% to 28% in the offshore island region. The HAA speciation obtained in this study was similar to the description of HAA levels in drinking water from the survey in Spain (Villanueva et al. 2003).

5. Cumulative frequency distribution

Figure 3 showed the cumulative frequency distribution of total THM and HAA5 collected in this study. During the two sampling durations in 2007, the 50th and 90th percentile of TTHM were 6.3 and 22.8 μg/L in the winter and were 8.3 and 33.8 μg/L in the summer, respectively. Most of the 172 samples taken during the two seasons met the current MCL for TTHM in Taiwan (80 μg/L). Moreover, only one and four measurements in winter and summer exceeded the current regulatory limit, respectively. In addition, all of the violations over the THM MCL were from Penghu islet (the offshore island county) because of the reasons described previously. The TTHM concentrations in Taiwan's finished water obtained in this study were lower than the results of the US Information Collection Rule (ICR) monitoring data which showed that the 50th percentile of TTHM in North Carolina was 41 μg/L (Shoaf and Singer 2007).

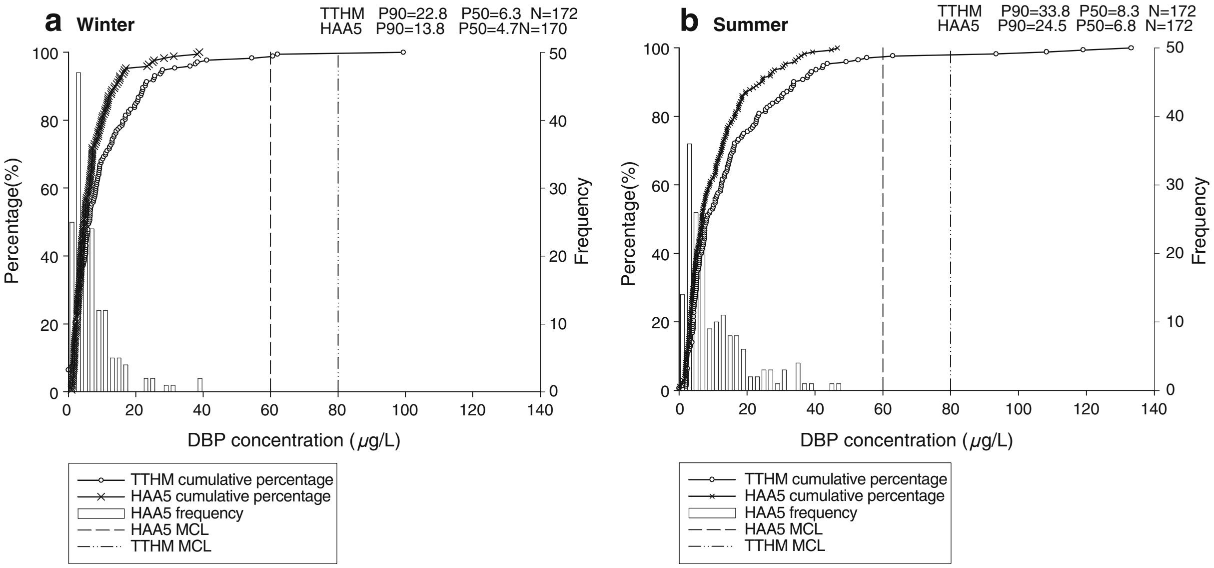

Fig. 3 Cumulative frequency distributions of HAA5 [sum of five haloacetic acids (MCAA, MBAA, DCAA, DBAA and TCAA)] and TTHM [total trihalomethanes (TCM, BDCM. DBCM and TBM)] concentrations in winter (**a**) and summer (**b**). *MCL* maximum contaminant level

The nationwide HAA concentrations were measured for the 86 major WTPs in Taiwan to set up the background database of HAA. Figure 3 demonstrated that the 50th percentiles of HAA5 were 4.7 μg/L in the winter and 6.8 μg/L in the summer. These results showed that 50% of HAA5 levels in drinking water served by the major utilities were below 7 μg/L under current treatment processes. The 90th percentiles of HAA5 were 13.8 μg/L in winter and 24.5 μg/L in summer. Even though the 90th percentile in the summer was higher than in the winter, most of the HAA5 levels were much lower than the MCL set by the US EPA. At a survey conducted in North Carolina (Shoaf and Singer 2007), the median of average HAA5 concentration was 27 μg/L, and about 2% of the 113 large systems examined had average HAA5 levels above MCL.

In addition, Fig. 3 further shows a difference in the frequency distribution for HAA5 between winter and summer. The cumulative percentages of both TTHM and HAA5 in summer increased more gently than in winter, and the frequency bars of HAA5 moved to the right-hand side and spread more widely in the higher concentration areas as well during the summer time. At the same time, the 50th and 90th percentiles in different seasons supported the seasonal DBP variations. Both the 50th percentiles from TTHM and HAA5 (8.3 and 6.8 μg/L) were greater than the values in winter (6.3 and 4.7 μg/L, respectively). The 90th percentiles of TTHM and HAA5 also increased significantly from 22.8 to 13.8 μg/L in winter to 33.8 and 24.5 μg/L in summer, respectively. The results in Fig. 3 suggested the seasonal variations of DBPs formation were due to significant variation of water temperature and raw water quality, as mentioned by Rodriguez et al. (2007a, b).

6. Relative occurrences of THMs and HAAs

Figure 4 shows the ratios of HAA5 to TTHM (a) and the ratios of HAA9 to TTHM (b). The ratio of the 50th percentiles of HAA5 to TTHM was 0.8 in both summer and winter seasons and indicated that the HAA5 were lower than TTHM concentrations for half of the water samples measured in this study. The 50th percentiles of the ratios of HAA9 to TTHM (Fig. 4b) were about 1.1 in both seasons. This observation demonstrated again that HAA9 was higher associated with TTHM than HAA5, and the total HAAs (by weight) concentration was higher than TTHM in drinking water. Compared to the seasonal variation for the ratios of HAAs to THMs, the higher ratio of HAA5 to

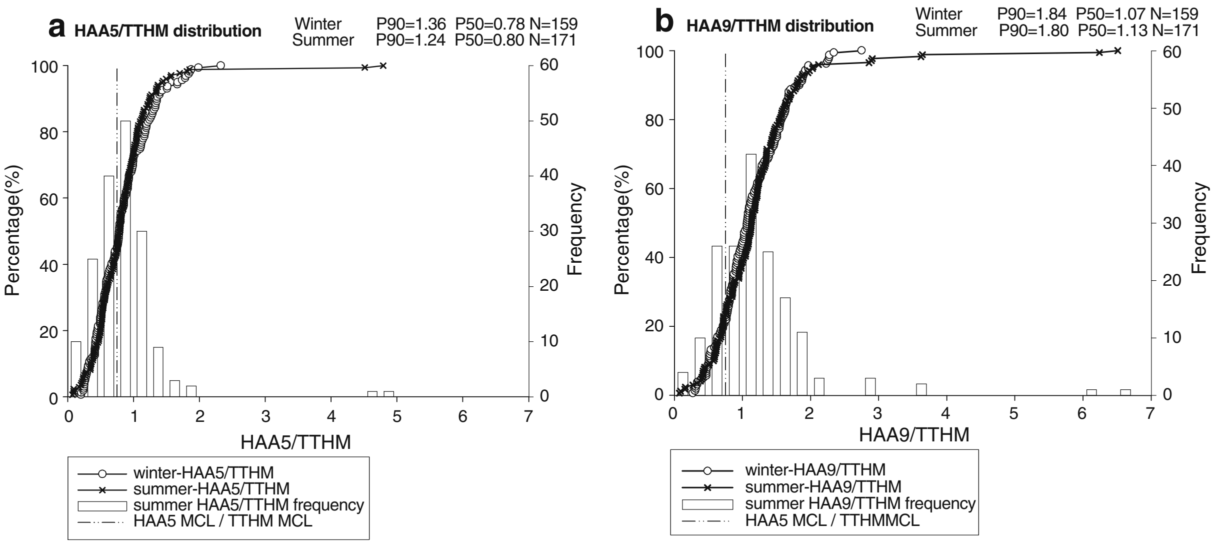

Fig. 4 Cumulative frequency distributions of the ratios of HAA5 to TTHM (**a**) and the ratios of HAA9 to TTHM (**b**)

TTHM (Fig. 4a) decreased in the summer. This might be associated with the biodegradation of some mono- or di-halogen HAAs in water where relatively lower concentrations of residual chlorine were observed in summer. The warmer water temperature in summer also enhanced the biological degradation of HAAs. However, the HAA9 which includes BCAA and the other three brominated trihaloacetic acids have shown their resistance to biodegradation (Baribeau et al. 2005).

Table 2 Regression analysis for THM and HAA

DBPs	Predict models	Regression coefficients		Statistical significance (*P* value)	Sample size (*n*)	Residuals	
		R square (r^2)	Adjusted *R* square (r_a^2)			Mean	SD
HAA5	$HAA5 = 4.909 \times NPDOC^{0.272}$	0.052	0.047	$P < 0.005$	172	0.000	0.997
HAA9	$HAA9 = 7.261 \times NPDOC^{0.235}$	0.042	0.037	0.007	172	0.000	0.997
HAA5	$HAA5 = 5.741 \times SUVA^{0.344}$	0.065	0.06	$P < 0.005$	172	0.000	0.997
HAA9	$HAA9 = 8.318 \times SUVA^{0.311}$	0.058	0.052	$P < 0.005$	172	0.000	0.997
HAA5	$HAA5 = 0.002 \times SUVA^{0.364} \times pH^{2.652} \times Temp^{0.872}$	0.138	0.121	$P < 0.005$	158	−0.061	0.942
HAA9	$HAA9 = 0.003 \times SUVA^{0.331} \times pH^{2.199} \times Temp^{1.111}$	0.144	0.128	$P < 0.005$	158	−0.067	0.951
HAA5	$HAA5 = 1.219 \times TTHM^{0.754}$ (Model 1)	0.658	0.657	$P < 0.005$	330	0.000	0.998
HAA9	$HAA9 = 1.824 \times TTHM^{0.735}$ (Model 2)	0.678	0.677	$P < 0.005$	330	0.000	0.998

Under this condition, the HAA9 is more resistant to biodegradation than HAA5, and there was no apparent difference on the ratios of HAA9 to TTHM between winter and summer.

Linear regression analysis between HAAs and THMs

Table 2 showed the correlations between HAAs and THMs based on the data collected in this study. If the THM levels could be used as an indicator of HAA levels in the water, the prediction model would be helpful for routine monitoring and management purposes for water utilities, since the analytical procedures for HAAs are both time and cost consuming due to the necessity of sample extraction and derivatization.

Logarithmic linear regression models (models 1 and 2 in Table 2) suggested the moderate and statistically significant correlations between TTHM and HAA5 or HAA9. Model 1 of HAA5 showed that HAA5 $= 1.219 \times \text{TTHM}^{0.754}$, $R^2 = 0.658$, $P < 0.005$. The model of HAA9 was similar to HAA5: HAA9 $= 1.824 \times \text{TTHM}^{0.735}$, $R^2 = 0.678$, $P < 0.005$. The variation of logTTHM could explain over 65% of the variability for logHAA5 or logHAA9, and most of the observed data were within the 95% confidence intervals of regressions, as shown in Fig. 5. Despite these intermediate R^2, Fig. 5 still demonstrated the similar trends that the more TTHM generated in water, the more HAAs are formed in the same system. Based on the information in Table 2 and Fig. 5, there was no apparent difference between the two models for prediction of HAA5 or HAA9 by TTHM concentrations. This may be attributed to the fairly low levels of bromide (less than 0.1 mg/L) in most of the source waters to form brominated trihaloacetic acids. As illustrated in Fig. 6, both the prediction models for HAA5 and HAA9 gave moderate fits when compared with the observed HAA levels. However, the consistence between the observed HAA9 and the predicted HAA9 was better than the prediction model for HAA5. This also supports the observation that the HAA9 should be considered for DBP control in order to prevent the underestimation of total HAAs.

It should be noted that both models described above gave lower ability to predict HAAs formation than the models developed by other surveys (Urano et al. 1983; Rathbun 1996; Uyak et al. 2007). Most of the published regression equations were based on laboratory scale chlorination experiments (DBPFP) where very high chlorine dosage was used. Besides, the data collected in

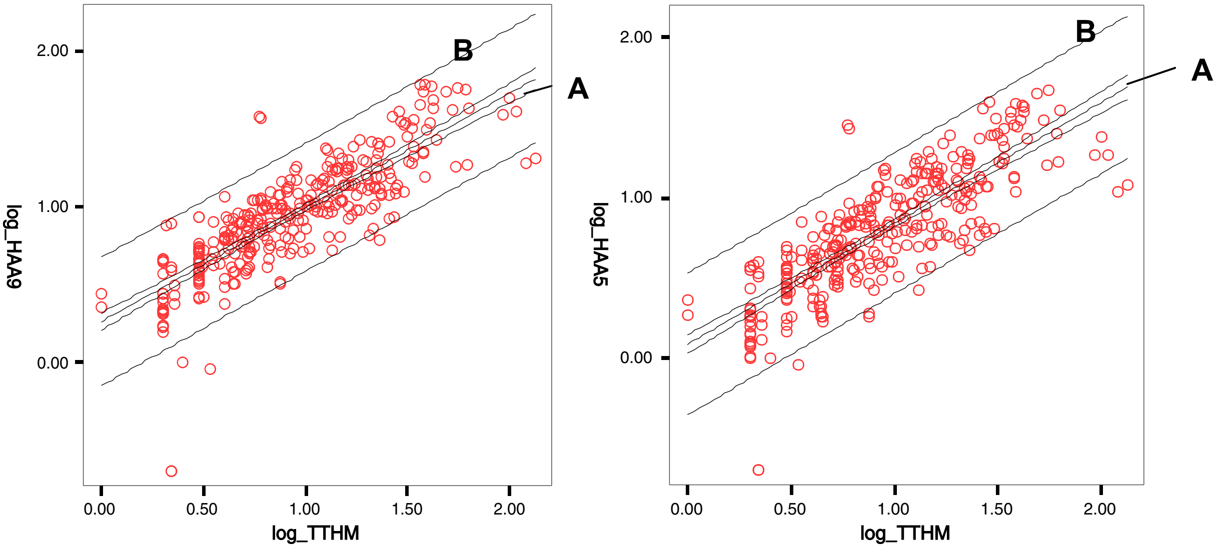

Fig. 5 Correlations between HAAs and TTHM concentration. *A lines* regression lines of model 1 and 2 in Table 2. *B lines* 95% confidence levels

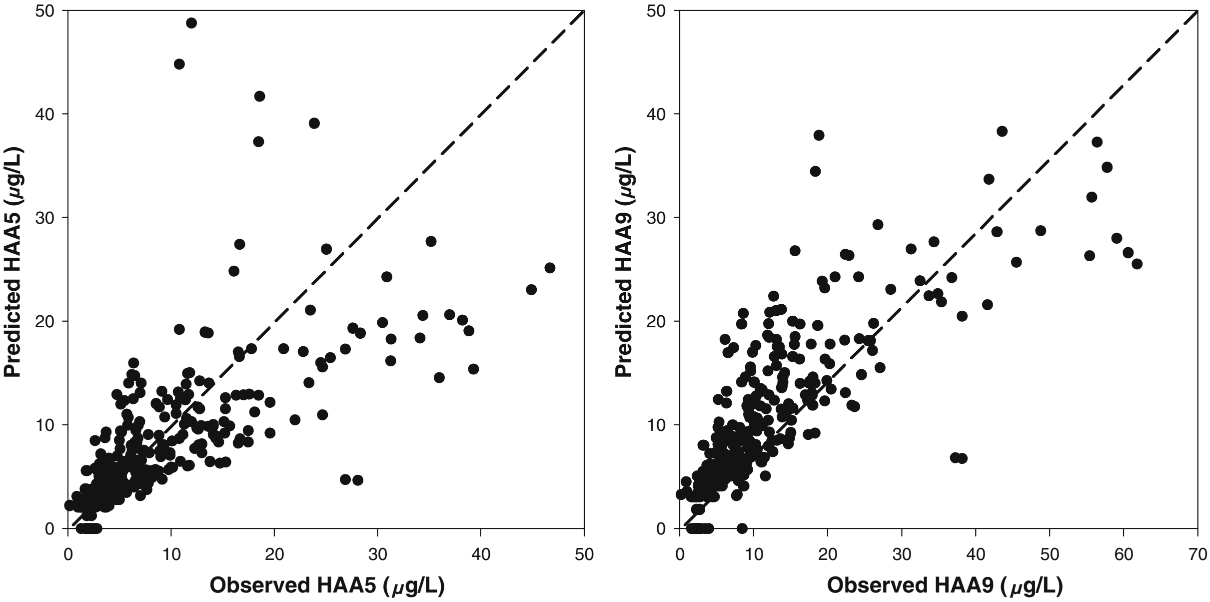

Fig. 6 Comparison between observed and predicted HAA concentrations. Predicted HAA concentrations are calculated from regression model 1 and 2 in Table 2

this study were from 86 different WTPs with different raw water qualities and various operation parameters. The complexity of DBP formation in different WTPs resulted in higher difficulty to develop a universally practical HAA-THM model. In addition, the results of this study also suggested that each WTP could establish their own model to obtain a more precise prediction for HAAs and TTHM for operational and managemental purposes.

Conclusions

This study collected water samples from 86 water treatment plants in Taiwan during February to March 2007 and July to August 2007 for THMs and HAAs analysis. The results showed that the HAA5 concentrations were from 1.0 to 38.9 μg/L in winter and from 0.2 to 46.7 μg/L in summer. For TTHM concentrations, the results showed ranges of ND-99.4 μg/L in winter and ND-133.2 μg/L in summer, respectively. Due to the various raw water qualities, it was observed that finished water in southern Taiwan and in the offshore island regions had higher DBPs concentrations. For samples taken from the offshore island WTPs, the relatively high bromide levels in source water resulted in the higher portion of brominated-DBPs in finished water. Other than the island region, DCAA (29.4–31.7%) and TCAA (25.3–27.6%) were the most abundant species for HAA in the main Taiwan island. The THMs species distribution in Taiwan has the similar trends as HAAs. The presence of relatively high bromide levels in offshore island WTPs shifted the HAA species to brominated-HAAs, it was observed that the total brominated trihaloacetic acids (BDCAA, DBCAA, and TBAA) accounted for 26–28% of the total HAAs for island WTPs, while only 10–14% of total HAAs in other areas were brominated trihaloacetic acids. This observation supports the conclusion that total HAAs (HAA9) should be considered for regulation of HAAs in drinking water. Logarithmic linear regressions showed that the THM levels in finished water could be used as an indicator of HAA levels in the same water, although only moderate associations were obtained for the correlations between THMs and HAA5 and HAA9.

Acknowledgements The authors thank Taiwan Water Corporation (TWC) for the financial support and the staffs of the 12 branches of TWC for their assistance in field sampling.

References

Austin, E. W., Parrish, J. M., Kinder, D. H., & Bull, R. J. (1996). Lipid peroxidation and formation of 8-hydroxydeoxyguanosine from acute doses of halogenated acetic acids. *Fundamental and Applied Toxicology, 31*(1), 77–82. doi:10.1006/faat.1996.0078.

Baribeau, H., Krasner, S. W., Chinn, R., & Singer, P. C. (2005). Impact of biomass on the stability of HAAs and THMs in a simulated distribution system. *Journal—American Water Works Association, 97*(2), 69–81.

Bove, F. J., Fulcomer, M. C., Klotz, J. B., Esmart, J., Dufficy, E. M., & Savrin, J. E. (1995). Public drinking-water contamination and birth outcomes. *American Journal of Epidemiology, 141*(9), 850–862.

Cantor, K. P., Hoover, R., Mason, T. J., & McCabe, L. J. (1978). Associations of cancer mortality with halomethanes in drinking-water. *Journal of the National Cancer Institute, 61*(4), 979–985.

Chang, H. H. (2004). *Analysis and distribution of haloacetic acids in drinking water of Taiwan* (p. 124). Institute of Environmental Health, College of Public Health. Taipei, Taiwan: National Taiwan University.

Chiang, P. C., & Chang, Y. Y. (2003). *The evaluation of microbial and potability standards in drinking water quality standards*. Taiwan EPA Project Report, EPA-92-J105–02–101, Taiwan (in Chinese).

Cicmanec, J. L., Condie, L. W., Olson, G. R., & Wang, S. R. (1991). 90-Day toxicity study of dichloroacetate in dogs. *Fundamental and Applied Toxicology, 17*(2), 376–389. doi:10.1016/0272-0590(91)90227-U.

Elshorbagy, W. E., Abu-Qdais, H., & Elsheamy, M. K. (2000). Simulation of THM species in water distribution systems. *Water Research, 34*(13), 3431–3439. doi:10.1016/S0043–1354(00)00231–1.

Giller, S., LeCurieux, F., Erb, F., & Marzin, D. (1997). Comparative genotoxicity of halogenated acetic acids found in drinking water. *Mutagenesis, 12*(5), 321–328. doi:10.1093/mutage/12.5.321.

Johnson, P. D., Dawson, B. V., & Goldberg, S. J. (1998). Cardiac teratogenicity of trichloroethylene metabolites. *Journal of the American College of Cardiology, 32*(2), 540–545. doi:10.1016/S0735-1097(98)00232-0.

Kato-Weinstein, J., Lingohr, M. K., Orner, G. A., Thrall, B. D., & Bull, R. J. (1998). Effects of dichloroacetate on glycogen metabolism in B6C3F1 mice. *Toxicology, 130*(2–3), 141–154. doi:10.1016/S0300-483X(98)00106-1.

Kramer, M. D., Lynch, C. F., Isacson, P., & Hanson, J. W. (1992). The association of waterborne chloroform with intrauterine growth-retardation. *Epidemiology (Cambridge, Mass.), 3*(5), 407–413. doi:10.1097/00001648-199209000-00005.

Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Sclimenti, M. J., et al. (2006). Occurrence of a new generation of disinfection byproducts. *Environmental Science & Technology, 40*(23), 7175–7185. doi:10.1021/es060353j.

Linder, R. E., Klinefelter, G. R., Strader, L. F., Suarez, J. D., & Dyer, C. J. (1994). Acute spermatogenic effects of bromoacetic acids. *Fundamental and Applied Toxicology, 22*(3), 422–430. doi:10.1006/faat.1994.1048.

Nelson, G. M., Swank, A. E., Brooks, L. R., Bailey, K. C., & George, S. E. (2001). Metabolism, microflora effects, and genotoxicity in haloacetic acid-treated cultures of rat cecal microbiota. *Toxicological Sciences, 60*(2), 232–241. doi:10.1093/toxsci/60.2.232.

Parrish, J. M., Austin, E. W., Stevens, D. K., Kinder, D. H., & Bull, R. J. (1996). Haloacetate-induced oxidative damage to DNA in the liver of male B6C3F1 mice. *Toxicology, 110*(1–3), 103–111. doi:10.1016/0300-483X(96)03342–2.

Rathbun, R. E. (1996). Regression equations for disinfection by-products for the Mississippi, Ohio and Missouri rivers. *The Science of the Total Environment, 191*(3), 235–244. doi:10.1016/S0048-9697(96)05266-7.

Rodriguez, M. J., Serodes, J., & Roy, D. (2007a). Formation and fate of haloacetic acids (HAAs) within the water treatment plant. *Water Research, 41*(18), 4222–4232. doi:10.1016/j.watres.2007.05.048.

Rodriguez, M. J., Serodes, J. B., Levallois, P., & Proulx, F. (2007b). Chlorinated disinfection by-products in drinking water according to source, treatment, season, and distribution location. *Journal of Environmental Engineering and Science, 6*(4), 355–365. doi:10.1139/S06-055.

Rook, J. J. (1974). Formation of haloforms during chlorination of naturals waters. *Journal Water Treatment and Examination, 23*(3), 234–243.

Sadiq, R., & Rodriguez, M. J. (2004). Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: A review. *The Science of the Total Environment, 321*(1–3), 21–46. doi:10.1016/j.scitotenv.2003.05.001.

Shoaf, D. R., & Singer, P. C. (2007). An analysis of monitoring data for the stage 1 disinfectants/disinfection byproducts rule. *Journal—American Water Works Association, 99*(10), 69–80.

Stacpoole, P. W. (1989). The pharmacology of dichloroacetate. *Metabolism: Clinical and Experimental, 38*(11), 1124–1144. doi:10.1016/0026-0495(89)90051-6.

Toth, G. P., Kelty, K. C., George, E. L., Read, E. J., & Smith, M. K. (1992). Adverse male reproductive effects following subchronic exposure of rats to sodium dichloroacetate. *Fundamental and Applied Toxicology, 19*(1), 57–63. doi:10.1016/0272-0590(92)90028-G.

TWEPA (2007). River Water Quality Statistics. In *Natonal Environmental Water Quality Information Network – 2007 Annual Report*. Taiwan Environmental Protection Agency. http://wqeng.epa.gov.tw/ (in Chinese).

Urano, K., Wada, H., & Takemasa, T. (1983). Empirical rate-equation for trihalomethane formation with chlorination of humic substances in water. *Water Research, 17*(12), 1797–1802. doi:10.1016/0043-1354(83)90202-6.

Urbansky, E. T. (2000). Techniques and methods for the determination of haloacetic acids in potable water. *Journal of Environmental Monitoring, 2*(4), 285–291. doi:10.1039/b002977g.

USEPA (1999b, EPA 815-R-99–013). Disinfection profiling and benchmarking guidance manual. In *Disinfection profiling and benchmarking guidance manual*. U.S. Environmental Protection Agency.

USEPA (2001a, EPA 816-F-01-007). National primary drinking water standards. In *National primary drinking water standards*. U.S. Environmental Protection Agency.

USEPA (2003, EPA 815-B-03-002). Method 552.3. Determination of haloacetic acids and dalapon in drinking water by liquid–liquid microextraction, derivatization, and gas chromatography with electron capture detection. In *Determination of haloacetic acids and dalapon in drinking water by liquid–liquid microextraction, derivatization, and gas chromatography with electron capture detection*. U.S. Environmental Protection Agency, Method 552.3.

Uyak, V., Ozdemir, K., & Toroz, I. (2007). Multiple linear regression modeling of disinfection by-products formation in Istanbul drinking water reservoirs. *The Science of the Total Environment, 378*(3), 269–280. doi:10.1016/j.scitotenv.2007.02.041.

Villanueva, C. M., Kogevinas, M., & Grimalt, J. O. (2003). Haloacetic acids and trihalomethanes in finished drinking waters from heterogeneous sources. *Water Research, 37*(4), 953–958. doi:10.1016/S0043-1354(02)00411-6.

Waller, K., Swan, S. H., DeLorenze, G. & Hopkins, B. (1998). Trihalomethanes in drinking water and spontaneous abortion. *Epidemiology (Cambridge, Mass.), 9*(2), 134–140. doi:10.1097/00001648-199803000-00006.

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology, 37*(20), 4702–4708. doi:10.1021/es030360x

WHO (1993). Guidelines for drinking-water quality. In *Guidelines for drinking-water quality*. Geneva: World Health Organization

Xie, S. G., Wen, D. H., Shi, D. W., & Tang, X. Y. (2006). Reduction of precursors of chlorination by-products in drinking water using fluidized-bed biofilm reactor at low temperature. *Biomedical and Environmental Sciences, 19*(5), 360–366.