

Health Risk Assessment from Haloacetic Acids Exposure in Indoor and Outdoor Swimming Pool Water

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Abstract

The concentrations of haloacetic acids (HAAs) in both indoor and outdoor swimming pools were assessed for cancer and non-cancer health risks with water samples collected during the summer and rainy seasons from two sources. Results showed that average concentrations of HAA5 (MCAA, DCAA, TCAA, MBAA, and DBAA) in both indoor and outdoor pools ranged from 74.28 to 163.05 μ g/L which was higher than USEPA and WHO water quality standards. Cancer and non-cancer risk values of HAA5 exposure from both swimming pool types were acceptable risks based on USEPA recommendation (10⁻⁶-10⁻⁴ and <1, respectively). The highest cancer and non-cancer risk values of HAA5 exposure were females for indoor pool and children for outdoor pool, respectively. Cancer and non-cancer risk values of HAA5 exposure from outdoor pool were higher than indoor pool and during the rainy season, respectively. Results indicated that monitoring and control of water quality and accumulated organic substance in swimming pools should be followed to maximize health risk reduction from HAA exposure.

Keywords: health risk assessment; Haloacetic Acids (HAAs); swimming pool; Thailand

1. Introduction

Swimming pools are used for recreational activities in many tropical countries and pool water should be disinfected to guarantee microbiological safety and hygienic water (Yang et al., 2016; Cheema et al., 2017). Waterborne diseases from pathogenic microorganisms in swimming pool water can be prevented and controlled using various types of disinfectants including chlorine, chloramine, chlorine dioxide, and ozone (Hang et al., 2016). Chlorine is the most widely used chemical disinfectant for swimming pool water because it is cheap and has high efficiency (Pan et al., 2014). However, the reaction of natural organic matter and human activity contaminants with the chlorine produces disinfection by-products (DBPs) (Cheema et al., 2017). Richardson (2008) identified more than one-hundred types of DBPs in swimming pool water including chloramines, haloacetonitriles (HANs), haloacetic acids (HAAs), trihalomethanes (THMs), chloral hydrates and nitrosamines (WHO, 2006; Chowdhury, 2015).

HAAs are the most commonly detected type of DBPs (Krasner et al., 2006) and are the public concern based on their potential genotoxicity and carcinogenicity to human health (Richardson et al., 2007). HAAs can be classified by nine compound types including bromochloroacetic acid (BCAA), chlorodibromoacetic acid (CDBAA), bromodichloroacetic acid (BDCAA), tribromoacetic acid TBAA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) (Simard et al., 2013; Tardif et al., 2016). The biological impacts on human health by DCAA and TCAA are assessed as probable (Group B2) and possible human carcinogens (Group C), respectively based on the regulation of The Integrated Risk Information System (IRIS); therefore, these chemicals should be strictly monitored (USEPA, 2003; Pals et al., 2011). The maximum contaminant level (MCL) of HAAs was 60 mg/L as the sum of five types of HAAs for drinking water based on the regulation of the United States Environmental Protection Agency (U.S. EPA) (EPA, 1998). Yang *et al.* (2016) determined that HAAs concentrations in swimming pool water were higher than in drinking water. Hence, HAA exposure among swimming pool users presented the possibility of human health problems.

Rattanapan et al. (2014) proposed health impact reduction from chemical exposure using the concept of health risk assessment. Panyakapo et al. (2008) and Lee et al. (2009) conducted health risk assessments for swimming pools with trihalomethanes (THMs) exposure. The formation of HAAs concentration was also affected by the type of swimming pool (Simard et al., 2013). Manasfi et al. (2017) identified HAAs concentrations in swimming pool water in European and developed countries. Data on the occurrence and health risk assessment of HAAs in various types of swimming pools in Thailand is limitation. Thus, the aim of this study was to assess HAAs concentrations in both indoor and outdoor Thai swimming pools. Results of the assessment of cancer and non-cancer health risks of HAAs exposure among various types of swimming pools were used to propose policy recommendations and implementations for decision-making in Thailand.

2. Materials and Methods

The health risk of HAAs exposure among swimming pool users was assessed and HAAs concentrations in indoor and outdoor pools were investigated. Cancer and non-cancer risk assessment of two pool types were assessed as follows:

2.1 Study cases of swimming pools

Two public swimming pools, one indoor and one outdoor, located in Hat Yai Municipality, Songkhla Province, Thailand were selected for study. The indoor pool located at Prince of Songkla University was 50 meters in length with tap water used as input. The outdoor pool located at the main stadium of Hat Yai Municipality, Songkhla Province was also 50 meters in length with tap water used as input. Ninety percent solid chlorine and sand filtration were the water treatments used in both these pools. Residual chlorine testing was followed up intermittently by the swimming pool operators. Water renewal in both pools was processed during the night (with filtration) to decrease accumulated contaminants.

2.2 Data collection and water sampling procedure

Data collection consisted of (1) user behavior and (2) the water quality of the swimming pools. Water was collected during the summer (March -April 2013) and rainy seasons (October - November 2016) and the behavior of swimming pool users was conducted using check lists. During water pool sampling, swimming pool users were investigated for weight, height, BMI and body surface area using standard procedures (Mosteller, 1987). The early, middle and end periods of the month were used to collect swimming pool water after six days of pool cleaning between 8.00 and 9.00 pm for a period of four months. Water was collected at five positions at 30 cm depth from each pool by grab sampling with a 1 liter bottle (Panyakapo et al., 2008). Raw water of each swimming pool (tap water) was collected as control. The water samples were added with 65 mg/L of ammonium chloride to inhibit the formation of HAAs and preserved at 4°C before analysis.

2.3 Analysis of water sample

Analysis of the water samples was based on the Standard Method for the Examination of Water and Wastewater 22th edition (APHA, AWWA, WEF; 2012). The pH and temperature were analyzed in situ by a pH meter (Horiba: Model D-12). A turbidity meter (Hach: Model 2100 P) was used to analyze the in situ turbidity concentration. The chlorine residual was measured by Iodometric titration technique and water samples passed through 0.45-µm membrane filter were used to measure the bromide ion content by ion chromatography. The water samples were passed through 0.7-um membrane filter following the standard 5910B Ultraviolet Absorption Method before UV absorbance at wavelength 254-nm analysis (UV-254) with UV/VIS Spectrophotometer (Jasco: Model V-530). Dissolved organic carbon (DOC) was measured by TOC analyzer (Shimadzu: Model TOC-L-CSN) based on the standard 5310B Combustion Method. Concentration of HAAs was measured by a micro-electron detector Agilent 7890 gas chromatograph (GC- μ ECD) with split less injection. The oven temperature program was as follows: 40°C for 0.5 min, first ramp of 10°C/min to 200°C (1 min). The temperature conditions of 230°C and 260°C were used to operate the injector and detector, respectively.

2.4 Exposure assessment

Potential HAAs exposure in the swimming pool water originated from multiple routes because of the different characteristics of swimming pool users (Pan *et al.*, 2014). In this study, the exposure assessment was categorized by three groups of swimming pool users including female, male, and children to assess cancer and non-cancer risks. Ingestion, dermal contact and inhalation routes of HAAs exposure were conducted. Chronic daily intake (CDI) and absorbed dose (AD) from different routes were assessed using equations (1), (2) and (3): (USEPA, 1989; Wang *et al.*, 2007; Chowdhury, 2013).

$$CDI_{ing} = \frac{(CW) (CR) (ET) (EF) (ED)}{(BW) (AT)}$$
(1)

$$AD = \frac{(CW) (CF) (SA) (PC) (ET) (EF) (ED)}{(BW) (AT)}$$
(2)

$$CDI_{inh} = \frac{(CA) (IR) (ET) (EF) (ED)}{(BW) (AT)}$$
(3)

Where: CDI_{ing} , CDI_{inh} and AD = chronic daily intake value (mg/kg-day) for ingestion and inhalation routes and absorbed dose for dermal contact, respectively; CW = chemical concentration in water (mg/L); CR = contact rate (L/h); ET = exposure time (h/day); EF = exposure frequency (day/year); ED = exposure duration (years); BW = body weight (kg); AT = average time (day); CF = conversion factor (L/cm³); SA = skin surface area available for contact (m²); PC= chemical-specific dermal permeability constant (cm/h); and IR= accidental intake of water (mL/h).

2.5 Health risk assessment

USEPA (1989) was recommended as the assessment method of cancer and non-cancer risk for chemical exposure. Health risk of carcinogenic exposure was assessed by the lifetime cancer risk equation (USEPA, 1989) as follows:

Lifetime cancer risk (LCR) = (Intake) \times (SF) (4)

Where Intake = CDI or AD of carcinogenic exposure value (mg/kg/day) and SF = slope factor of carcinogen [(kg.day).mg⁻¹]. The values of health risk for carcinogenic exposure are accepted and unaccepted if LCRs are the range of 10^{-6} - 10^{-4} and more than 10^{-4} , respectively.

The hazard quotient (HQ) was used to assess the health risk of non-carcinogenic exposure as follows (USEPA, 2009):

$$HQ = Intake/RfD$$
(5)

Where Intake = CDI or AD of non-carcinogenic exposure value (mg/kg/day) and RfD = reference dose of non-carcinogen [(kg.day).mg⁻¹]. A non-carcinogenic effect is a concern if HQ > 1 and is no concern if HQ <1 acceptable level.

3. Results and Discussion

3.1 Water quality parameters in various swimming pool types

Table 1 shows the parameters of water quality in both indoor and outdoor swimming pools. The result identified that pool water had a higher pH, temperature, chloride residual, and the aromaticity of organic compounds (DOC and UV 254) was higher than in tap water sample. Non-detection was found in bromide ion concentrations in all samples. This result concurred with Zhang *et al.* (2011) who determined that the concentrations of bromide ion in tap water and swimming pools were relatively low (<50 µg/L). The high concentration of organic compounds represented aromaticity contamination from human activity (Hang *et al.*, 2016).

Temperature and turbidity in all samples were significantly higher in the summer season than during the rainy season and resulted from increased reaction of high turbidity and temperature with added chorine. Thus, the chorine residual of the water sample was less concentrated in the rainy season (Richardson, 2008). The DOC and UV 254 concentrations of all water samples in the summer season were higher than during the rainy season. Similarly, the finding of Chowdhury (2013) reported that DOC and UV-254 showed higher concentrations ($0.92\pm0.21 \text{ mg/L}$, 0.59 -1.47 mg/L) than in the rainy season ($0.0585\pm0.01 \text{ cm}^{-1}$, $0.0322\pm0.01 \text{ cm}^{-1}$).

Regarding pool types, the outdoor swimming pool water had higher turbidity, DOC and UV 254 than the indoor pool. Cardador and Gallego (2011) mentioned that outdoor pool water consisted of more and different types of precursors than indoor pool water. Wind, grass, soil, leaves, insects, rain and temperature from the external environment may enhance the contamination level of water in outdoor pools.

Doromotora	Season	Water Sources				
Parameters		Tab Water I	Indoor pool	Tab Water II	Outdoor pool	
pН	Summer	6.49±0.30	7.64±0.23	6.41±0.19	7.59±0.18	
	Rainy	6.33±0.12	7.60 ± 0.28	6.45±0.21	7.45±0.19	
Temperature (°C)	Summer	28.92±0.77	27.43±0.63	28.70±0.62	29.12±0.12	
	Rainy	27.57±0.93	26.50±0.36	28.11±1.04	27.68±0.97	
$Cl^{-}(mg/L)$	Summer	0.25±0.12	1.78±0.32	0.80 ± 0.32	0.96 ± 0.05	
	Rainy	0.17±0.05	2.65±0.59	0.35±0.16	1.42 ± 0.38	
Turbidity (NTU)	Summer	3.43 ± 1.48	2.98±0.33	2.78±0.21	3.18±0.22	
	Rainy	2.90±0.25	1.53±0.39	1.78 ± 0.53	1.44±0.19	
$Br^{-}(mg/L)$	Summer	ND	ND	ND	ND	
	Rainy	ND	ND	ND	ND	
DOC (mg/L)	Summer	1.43 ± 0.51	1.90 ± 0.83	1.62 ± 0.52	9.11±0.52	
	Rainy	0.88 ± 0.28	0.95±0.11	1.33 ± 0.75	8.60 ± 0.60	
$UV254 (cm^{-1})$	Summer	0.0392 ± 0.02	0.0585 ± 0.01	0.0662 ± 0.04	0.1059 ± 0.10	
	Rainy	0.0259 ± 0.02	0.0322 ± 0.01	0.0472 ± 0.03	0.0573 ± 0.02	

Table 1. Average water quality parameters of samples from various swimming pool types

Note: ND: Non-detectable; Tab Water I = raw water of indoor pool; Tab Water II = raw water of outdoor pool

3.2 HAAs concentrations in difference swimming pool types

The average HAA5 concentrations (MCAA, DCAA, TCAA, MBAA, and DBAA) of tap water I and II in the summer and rainy seasons were 1.78 and 1.64, and 2.64 and 0.64 μ g/L, respectively (Table 2). For swimming pool types, the average HAA5 in the indoor and outdoor pools in the summer and rainy seasons were 151.35 and 74.28, and 163.05 and 100.98 µg/L, respectively. Concentrations of MBAA and DBAA were not found in the tap and swimming pool water because of low bromide ions in the water source (Richardson, 2008). These results implied that HAA5 concentrations in tap and pool water were lower and higher than the USEPA and WHO quality standard. USEPA (1998; 2006) and WHO (2006) recommended the drinking water standard of HAA5 concentration (Table 2) as $<60 \ \mu g/L$ and $<80 \ \mu g/L$, respectively for maximum contaminant level (MCLs).

Results of the average concentrations of HAA5 in swimming pool water are presented in Table 2 and were higher than the tap water samples (more than 74 times). The DBP occurrence was generated from DBP precursors and human origin including urine, hair, saliva and body care products (Simard *et al.*, 2013). Swimming pool water can accumulate relatively high levels of HAA5 compared to tap water.

All water samples showed HAA5 concentrations in the summer season as significantly higher than the rainy season. Chowdhury (2013) specified that higher concentrations of organic matter, residual chlorine and temperature during the summer season can accelerate the reaction of organic matter and chlorine to generate higher DBP concentrations. The HAA5 concentrations between indoor and outdoor swimming pool water investigated that HAA5 concentrations of all samples in outdoor pool were significantly higher than indoor pool. This result was consistent with the characteristic of water pool quality (3.1). Simard *et al.* (2013) also mentioned that water in outdoor pools contained on average two times more HAA5 than water of indoor pool with statistically significant differences.

3.3 Health risk assessment

3.3.1 Cancer risk assessment by life time cancer risk (LTC)

Information required for LTC are slope factors rated from the data of many models and approximating 95% confidence limits (Pan et al., 2014). USEPA (2014) identified that the slope factor displayed a 95-percentile upper-bound lifetime cancer risk from exposure to a carcinogen. LTC slope factors were assessed for two HAAs as DCAA and TCAA. The slope factors of HAA5 for the ingestion route only were 5 x 10^{-2} mg/kg/day for DACC and 7 x 10^{-2} mg/kg/day for TCAA. For the inhalation route, 1.4 x 10⁻⁶ mg/kg/day was the slope factor of DCAA (USEPA, 1991; RAIS, 2009; IRIS, 2009). The exposures of ingestion, dermal skin and inhalation routes were then used to assess LTC as equation (4) with the parameter values for chronic diary intake or and absorbed dose in Table 3. The result in Fig. 1 showed that the range of values of overall LTC for HAAs exposures to swimming pool water were 8.1×10^{-6} -5.7×10⁻⁵. For each pool user group, the high, middle and low risks of LTC values for DCAA, TCAA and HAA5 the indoor and outdoor

	G	Water Sources				Maximum contaminant levels, (MCLs) (μg/L)	
HAAS	Season	Tab	Indoor	Tab	Outdoor	USEPA*	WHO**
		Water I	pool	Water II	pool		
MCAA (µg/L)	Summer	0.54	30.22	0.98	39.30	-	-
	Rainy	0.48	21.35	0.97	23.18		
MBAA (µg/L)	Summer	ND	ND	ND	ND	-	-
	Rainy	ND	ND	ND	ND		-
DCAA (µg/L)	Summer	0.60	54.12	0.65	59.05	-	50
	Rainy	0.55	27.29	0.13	38.23		
TCAA (µg/L)	Summer	0.63	67.01	1.01	64.70	-	100
	Rainy	0.61	25.65	0.81	39.57		
$DBAA(\mu g/L)$	Summer	ND	ND	ND	ND	-	-
	Rainy	ND	ND	ND	ND		-
HAA5 (µg/L)	Summer	1.78	151.35	2.64	163.05	60	80
	Rainy	1.64	74.28	0.64	100.98		

Table 2. Average HAAs concentrations of samples from various swimming pool types

Note: ND: Non-detectable; Tab Water I = raw water of indoor pool; Tab Water II = raw water of outdoor pool * USEPA, 1998; USEPA, 2006

**WHO, 2006.



Figure 1. Cancer risk values (Life time cancer) of DCAA, TCAA and HAA5 for indoor and outdoor pools

Derometera	Values			Linita	Courses
Parameters	Child Male Female		Female	Units	Sources
Contact rate (CR)	0.021	0.021	0.049	L/h	USEPA (2009)
Conversion factor (CF)	0.001	0.001	0.001	L/cm ³	USEPA (1989)
Exposure duration (ED)	30	30	6	years	USEPA (1989)
Exposure frequency (EF)	240	240	240	day/year	Check list
Exposure time (ET)	60	60	60	min/day	Check list
Skin surface area	$15,700^{*}$	$17,900^{*}$	$10,470^{**}$	m^2	*NECTEC (2009) and
available for contact (ST)					**USEPA (2009)
Average time (AT)	25,550	25,550	25,550	day	USEPA (1989) and
					Lee et al. (2009)
Body weight (BW)	57.4*	68.9^{*}	29^{**}	kg	* NECTEC (2009) and
, , ,				-	**USEPA (2009)

Table 3. Parameter values for chronic diary intake and absorbed dose

pool water in summer and rainy seasons with the three exposure routes were female, male and children, respectively. In addition, results indicated that dermal contact was the main route of HAAs exposures from swimming pool water. This finding was consistent with Chowdhury (2015) and ECETOC (1994) mentioned that during swimming HAAs can be absorbed by the human skin and impacted on health. In summer season, LTC values of DCAA, TCAA and HAA5 were significantly higher than during the rainy season for both swimming pools. Increasing concentration of DBPs originated in the warm season and increased human risk exposure (Chowdhury, 2015). LTC risk values in outdoor swimming pool were also significantly higher than indoor pool water because UV sunshine increased DBP exposure values in outdoor pools (Simard et al., 2013). However, all LTC values were acceptable in the range of 10^{-6} and 10^{-4} based on the USEAPA recommendation.

3.3.2 Non-cancer risk assessment by hazard quotient (HQ)

The HQ calculation identified the health risk for non-cancer exposure as the ratio of potential exposure against expectation level of no adverse impact (Liang et al., 2016). Chowdhury (2015) noted that required information for HQ calculation was reference doses (RfDs), which present the safe dose that can be ingested without any adverse effect (USEPA, 2014). The RfDs of MCAA, DCAA and TCAA are 4×10^{-3} , 3×10^{-3} and 2 x 10^{-2} g/kg/day, respectively. Next, exposures to ingestion, dermal skin and inhalation routes were used to assess the non-cancer risk as equation (5) with the parameter values for chronic diary intake or and absorbed dose in Table 3. Results in Fig. 2 indicated that risk assessment values of non-cancer in indoor and outdoor swimming pool water were similar to cancer risk with a range of 3.31×10^{-2} and 1.72×10^{-1} . The highest, middle and lowest values of non-cancer risk

among swimming pool users were female, children, and male, respectively. In summer season, all non-cancer risk values were significantly higher than during the rainy season and all non-cancer risk values in outdoor pool were also significantly higher than in indoor pool. However, all non-cancer risk values in both indoor and outdoor pools during summer and rainy seasons in all user groups were acceptable based on the USEPA recommendation.

3.4 Recommendations for health risk reduction

The values of cancer and non-cancer risk assessment of HAA5 exposure in indoor and outdoor pools were acceptable. However, most HAA5 concentrations were higher than the water quality standard. Hence, a recommendation of health risk reduction to HAAs exposure should be proposed for long-term prevention of human health impacts. Approaches of health risk reduction were made for swimming pool management and swimming pool users as follows:

3.4.1 Recommendations for swimming pool management

Results from swimming pool water quality identified that concentrations of DOC and UV-254 were influential factors of HAAs formation and higher in the summer season. Hence, (1) DOC should be reduced in tap and swimming pool water to control the precursor of HAAs formation, (2) temperature should be reduced in swimming pools to control the reaction of HAAs formation, (3) daily monitoring of water quality in taps and swimming pools should be initiated, including pH and chlorine residual to reduce the chance of HAAs formation, (4) water in the swimming pools should be changed regularly to reduce organic substances, and (5) addition of sand and system in the water treatment of the swimming pool will remove the suspended solids.



Figure 2. Non-cancer risk values (Hazard quotient) of TCAA, DCAA, TCAA and HAA5 for indoor and outdoor pools

3.4.2 Recommendations for swimming pool users

The results of personal and behavior factors identified that (1) swimming suits should cover the skin to reduce water contact, (2) frequency and time period of swimming should be reduced to prevent skin exposure, (3) promotion campaigns to ban skin lotions for swimming pool users, and (4) taking a shower before using the pool.

4. Conclusions

The following perorations were made: (1) the average concentrations of HAA5 (MCAA, DCAA, TCAA, MBAA, and DBAA) in indoor and outdoor swimming pools were higher than water quality standards of USEPA with the range of 74.28 to 163.05 µg/L. (2) Cancer and non-cancer risk values of HAA5 exposure in both indoor and outdoor swimming pools were lower than the acceptable value of risk recommendation by USEPA. (3) Cancer and non-cancer risk in outdoor swimming pools and during the summer season were highest followed by indoor swimming pools and rainy season, respectively. (4) The female and children groups of swimming pool users had the highest risk of HAA5 exposure from indoor and outdoor pools, respectively. Finally, precursor control and monitoring of HAAs formation as DOC and UV 254 concentration should be proposed for health risk reduction.

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