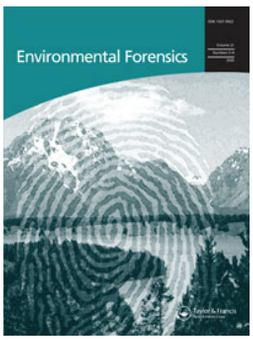

Environmental Forensics

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/uenf20

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To cite this article: Edip Avsar, Dilara Deniz Avsar & Sukru Hayta (2020) Evaluation of disinfection by-product (DBP) formation and fingerprint in a swimming pool in Bitlis/Turkey: a case study, Environmental Forensics, 21:3-4, 375-385, DOI: 10.1080/15275922.2020.1772413

To link to this article: https://doi.org/10.1080/15275922.2020.1772413

ENVIRONMENTAL FORENSICS
2020, VOL. 21, NOS. 3–4, 375–385
https://doi.org/10.1080/15275922.2020.1772413

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Evaluation of disinfection by-product (DBP) formation and fingerprint in a swimming pool in Bitlis/Turkey: a case study

Edip Avsar[a], Dilara Deniz Avsar[b], and Sukru Hayta[a]

[a]Environmental Engineering Dept, Bitlis Eren University, Bitlis, Turkey; [b]Institute of Science, Bitlis Eren University, Bitlis, Turkey

ABSTRACT

In this study, water quality parameters and disinfection by products (DBPs) were monitored and correlations between them were statistically investigated in a swimming pool in the province of Bitlis in Turkey. Risk assessment was then performed for trihalomethanes (THMs) and haloacetic acids (HAAs) in the context of public health. According to results, the carbonaceous organics (maximum total organic carbon (TOC): 3.89 mg/L) and nitrogenous (maximum total nitrogen (TN): 6.84 mg/L) substances came from swimmers as the precursor compounds for the formation of DBPs. Pool water free chlorine concentration varied depending on the manual dosage (between 0 to 2.2 mg/L) and sometimes exceeded the Turkish limits (1-1.5 mg/L). This situation increased DBPs formation. Bromide concentration detected in pool water can reach up to 15-fold the value in groundwater. This provides the basis for formation of brominated DBPs which are more carcinogenic than chlorinated species. The THM_4 (mean: 85.4 μg/L) and bromoform (mean: 70.2 μg/L) concentrations were higher than those obtained in most countries. Low nitrogenous compounds limited the haloacetonitrile (HAN) production (mean: 3.52 μg/L). Significant differences were detected between HAA_5 and HAA_9 concentrations (mean: 181 and 219 μg/L respectively) and this difference came from high amounts of brominated HAA species. Other DBPs that cannot be detected on species basis varied and constituted mean 53.5% of adsorbable organic halogens (AOX). This situation creates uncertainty in terms of health hazards. According to Pearson correlations, there were significant correlations between AOX formation and TOC, TN, conductivity, total chlorine, nitrate and temperature. This indicates that DBPs formation was mainly influenced by the precursors in the water and the physical conditions in the pool. Therefore these parameters are the fingerprint of DBP formation in the studied pool water and negative or positive changes in these parameters directly affect DBP generation. It is very important to keep them under constant control in pool water. According to the risk assessment results, HAA concentration in the pool was found to have the potential to pose a risk to public health. The study provides fingerprinting information for DBP formation under uncontrolled pool conditions.

KEYWORDS

Disinfection by-product fingerprint; chlorination; pool water; SPSS; public health risk assessment

1. Introduction

Different disinfection methods are employed to remove pathogens in water systems either individually or in combination (National Academy of Sciences, 1977; Tunay, 1996; Sawyer et al., 2002; Ilyas et al., 2018).

Chlorination is the most common method for disinfection of water resources. However, formation of halogenated hydrocarbons as a result of the chlorination process and the fact that some of these by-products have carcinogenic effects in animal experiments have led to introduction of alternative disinfectants and procedures (National Academy of Sciences, 1977; Tech Brief, 1996; Sawyer et al., 2002; Uyak et al., 2014).

In recent years, quantification and monitoring of by-products formed as a result of chlorination in swimming pools has gained significance in the context of public health. The pool in this study was filled with groundwater that included bromide and was exposed to manually applied and irregular dosages of chlorine. The variations in the precursor (body fluids) concentration in the pool reflect the level of responsibility and cultural habits of the swimmers, and along with the aforementioned properties that collectively affect the type and amount of disinfection by products

CONTACT Edip Avsar edipavsar@hotmail.com Environmental Engineering Dept, Bitlis Eren University, Bitlis, Turkey
Supplemental data for this article can be accessed at https://doi.org/10.1080/15275922.2020.1772413

Table 1. Regulations imposed by different countries and organizations about the amount of residual chlorine and other parameters in pool water (Avsar 2018).

	Regulation				
Parameters	World Health Organization (WHO) (Anonymous, 2006)	US Environmental Protection Agency (USEPA) ANSI, 2019)	China (National hygiene standard for swimming areas) (Wei et al., 2018)	Turkey (Regulations on the health principles and conditions of swimming pools) (MOFH, 2011)	Canada Toronto Public Health (Anonymous, 2019)
Disinfectant used	Free chlorine Combination of free chlorine and other methods (ozone, UV, etc.)	Free chlorine Chlorinated isocyanates	Free chlorine	Free chlorine	Free chlorine or bromine
Free chlorine residue (mg/L)	1–3 0.5–3	0.6–1 1–2	0.3–0.5	1–1.5	min. 2
pH	7.2–7.8	7.2–7.8	6.5–8.5	6.5–7.8	7.2–7.8
Total alkalinity ($mgCaCO_3/L$)		60–180		30–180	80–120
Temperature (°C)	26–30	26–28	22–26	26–28	
Nitrate (mg/L)				50	
Hardness ($mgCaCO_3/L$)		150–1000			100–450
Oxidation reduction potential (ORP) (mV)					600–900
Turbidity (NTU)			5		

(DBPs) formed in the pool, these ultimately make the pool an excellent research topic. For this purpose, the aforementioned pool, which was open for public use in the center of the province of Bitlis, was investigated between July to September 2017. DBPs of the swimming pool were monitored during the season, the effects of water quality on by-product formation were determined, and the effects of the by-products on public health were evaluated.

2. Literature review

Management of swimming pools is shaped by factors such as the ease and cost of replacement water, heating and treatment. The safety of pool water is always the most important issue for swimmers and operators. Chlorine is the most commonly used disinfectant for this purpose. Solid ($Ca(OCl)_2$) or liquid (NaOCl) forms are widely applied (Zhang et al., 2015; Yang et al., 2016; Yue et al., 2016; Cheema et al., 2017).

In order to ensure effective disinfection, there must be a suitable amount of residual chlorine in the pool water (Zhang et al., 2015).

Various limitations on residual chlorine and other parameter amounts are given in Table 1.

Chlorination of swimming pools leads to the formation of many potentially toxic DBPs, including trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs) (Uyak et al., 2008; Krasner, 2009; Avsar, 2013; Han et al., 2017).

THMs are the first group identified and are classified as possible carcinogens. HAAs are another common DBP group. Because of their high toxicity, there is increasing concern regarding health problems caused by ingestion or dermal and respiratory exposure. Some toxicological studies show the cytotoxic, genotoxic, mutagenic and teratogenic effects of HAAs on various cells. In addition to these by-products, more than 100 other DBPs such as chloramines, HANs, chloral hydrate (CH) and nitrosamines were identified in pool water (Yang et al., 2016; Cheema et al., 2017).

The importance of volatile DBPs resulting from chlorination is increasing because of the concern that they cause respiratory problems in swimmers and pool staff. Exposure to DBPs in general is in the form of dermal absorption, inhalation or accidental ingestion. Exposure is reported to result in increased risk of cancer, eye irritation, asthma and disorder of the endocrine system. Additionally, many DBPs that form after chlorination are genotoxic. Nevertheless, studies investigating the mutagenic or genotoxic potential of swimming pool water are quite limited (Villanueva and Ribera, 2012; Zhang et al., 2015; Yue et al., 2016; Cheema et al., 2017).

DBPs formed in pools exhibit different characteristics in comparison to DBPs formed in drinking water. These characteristics depend on a number of factors such as organic precursors of human origin, water temperature, differences in disinfectant doses and the form of exposure (Hang et al., 2016).

In pool water, precursor compounds from swimmers were noted to be more important in comparison to water-borne precursor (e.g., dissolved

Table 2. Results reported for DBP values in pool water in various countries (Zhang et al., 2015).

Country	Pool type	DBP type	Average concentrations (μg/L)
China	14 outdoor and indoor swimming pools	THMs	33.8
UK	8 indoor swimming pools		132.4
US	20 indoor swimming pools		63
Korea	30 indoor swimming pools		20.3 (Chloroform only)
France	15 indoor swimming pools		25.9
Canada	15 indoor swimming pools		63.7
	30 indoor swimming pools		97.9
Italy	20 indoor swimming pools		36.9
Germany	3 samples from one swimming pool		7.1–24.8
China	14 outdoor and indoor swimming pools	HAA_9	109.1
US	20 indoor swimming pools		960
Canada	15 indoor swimming pools		412.9
	30 indoor swimming pools		807.6
Italy	20 indoor swimming pools		164
China	14 outdoor and indoor swimming pools	HAN_4	3.2
		CH	30.1
		1,1-Dichloro-2-propanone (1,1-DCP)	0.3
		1,1,1-Trichloro-2-propanone (1,1,1-TCP)	0.6

organic matters) compounds. The potential for HAA formation from these precursor compounds was found to be higher than potential THM formation. This is due to the fact that HAAs are less volatile in comparison to THMs, and thus, it is more difficult for them to diffuse from water into air. It was determined that there is a positive correlation between the total amount of organic carbon (TOC) content, the amount of disinfectant and the number of swimmers in the pool with the amount of DBPs. One of the reasons for the wide variations reported in DBP concentrations in different pools and countries is that the number of swimmers and the legal standards for free chlorine residue in the pools differ from country to country (Yue et al., 2016; Manasfi et al., 2017).

Many studies were conducted to determine the amount of DBPs in pool waters in developed countries. However, most of these studies targeted THMs, and very few reported HAAs, CH, haloketones, nitrogenous DBPs (HANs, etc.) and halonitromethanes (HNMs). When DBP values across various studies are compared, it is generally observed that the reported values vary within a wide range. The data gathered from a spectrum of studies are listed in Table 2. In general, HAA concentrations measured in the same pools were higher than THMs, and dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the most significant types of HAA (Zhang et al., 2015).

DBPs may be reduced by pool water replacement or different treatment methods. In open swimming pools, free chlorine is rapidly decomposed by strong sunlight. Circulation of the swimming pool water increases accumulation of DBPs. Due to these drawbacks of chlorine, organic-based alternative disinfectants such as trichloroisocyanuric acid (TCCA) and bromo chloro-dimethylhydantoin (BCDMH) are used for disinfection of pools. TCCA is reported to stabilize halogens, provide a slower breakdown of free chlorine and form lower amounts of DBPs in comparison to free chlorine. After chlorination, it is also possible to remove chloramines by UV treatment. However, contradicting results were previously reported regarding the increasing or decreasing effect of UV usage on the amount of THMs (Yang et al., 2016; Cheema et al., 2017).

Exposure to DBPs in chlorinated water is an important public health problem because it increases the risk of developing colon, rectal and bladder cancer (Sayess et al., 2017).

The mutagenicity and toxicity of pool water was demonstrated to be higher than drinking water in various studies. In Thailand, the lifelong cancer risk from DBPs in pool water was calculated to be 7.53×10^{-4}. In another study conducted in Korea, the estimated risk of life-long cancer due to respiratory exposure to THMs was found to be between 7.77×10^{-4} and 1.36×10^{-3}. In a study conducted in Taiwan, the risk of cancer in male and female swimmers was reported to vary between 6.87×10^{-5} and 5.46×10^{-5}, and respiratory exposure was noted to be the most important source constituting more than 99% of the risk (Hang et al., 2016).

3. Materials and methods

3.1. Sampling point and procedure

The study was carried out at a public indoor swimming pool in the province of Bitlis in Turkey between July and September 2017 in the season when it was used most intensely. The pool has a volume of 778.75 m^3 and is filled with groundwater. Water in the system is continuously circulated, and coarse and

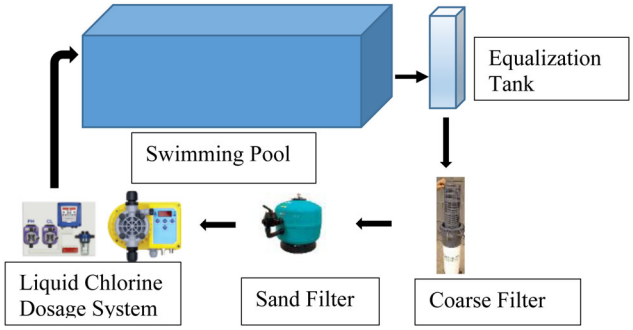

Figure 1. The operating schema of the pool.

fine particles are filtered. The pool has a pH-controlled liquid chlorine dosing system. However, the system pumps were not operated due to a malfunction. Solid chlorine ($Ca(ClO)_2$) is dosed daily by hand into the system. The process flow diagram for the system is given in Figure 1.

Sampling for the study was performed from the midpoint of the pool at a depth of 30 cm and at least one hour after chlorination. The pH, conductivity, temperature, free and total chlorine, and oxidation-reduction potential (ORP) measurements were performed on site. After sampling, the chlorine in the sample was inactivated with sodium thiosulfate, transferred to the laboratory, and subsequent analyses were completed on the same day (Avsar et al., 2014, 2015; Avsar and Toroz, 2018).

3.2. Analysis methods

The parameters that were measured and the devices and methods that were utilized are summarized in Table 3 (Avsar, 2018; Kilic, 2018).

3.3. Statistical analysis

The statistical evaluation of the relationships between water quality parameters and occurrence of DBPs was performed by using SPSS software. Pearson correlation analysis was used for this purpose.

Throughout the analyses, a P-value of <0.01 was considered highly significant, and P-value of <0.05 was considered significant for the correlations between two variables (Zhang et al., 2015).

4. Results

4.1. Pool water quality and DBP formation

Chemical water quality of pool water has recently been a major concern. In this context, many studies were carried out in US and Europe. A significant elevation in the formation of DBPs in pool waters and spas (between 610 and 900%) compared to raw water fed to pools indicates that DBPs formation is an important public health issue (Carter and Joll, 2017). Table 4 shows the comparison between the quality of the groundwater used to feed the pool and the quality of the pool water. As seen in Table 4, the carbonaceous and nitrogenous organic substances which are the leading compounds in the formation of DBPs and the UV_{254} parameter which characterizes them were significantly higher in pool water. This means that the amount of DBPs formed in the pool water was much higher than the amount that occurred in groundwater. It also shows that carbonaceous and nitrogenous precursor compounds from swimmers which have the potential to produce DBPs began to accumulate in the pool.

The amount of free chlorine in the swimming pool water varied depending on the manual dosage application and the values sometimes exceeded the Turkish limit value which is given in Table 1. The amount of combined chlorine was also thought to vary in respect to the amount of the nitrogenous compounds in the water.

The water qualities of tap water and pool water were compared in the literature. The concentration of TOC ranged from 0.3 to 1.4 and from 0.5 to 7.0 mg/L in tap water and pool water, respectively. Nitrate nitrogen (NO_3^--N) was higher in pool water (6.6–23.8 mg/L) than tap water (1.1–1.9 mg/L). Similarly, TN was higher in swimming pool water (3.6–12.3 mg/L) than tap water (0.1–0.3 mg/L). The temperature of the pool water (25–35 °C) was higher than that of tap water (1.0–23 °C) (Ilyas et al., 2018).

In another study, water quality parameters in indoor swimming pools were monitored (Zhang et al., 2015). In three indoor pools where free chlorine was used as a disinfectant, the following range and mean values were gathered; total chlorine: 0.75–2.00 mg/L (mean: 1.18), free chlorine: 0.34–1.73 mg/L (mean: 0.81), TOC: 6.09–16.18 mg/L (mean: 11.68), UV value: 0.03–0.07 cm^{-1} (mean: 0.05), pH: 7.60–8.47 (mean, 8.11), nitrate: 23.29–48.49 mg/L (mean: 32.22), and total organic nitrogen: 0.38–3.42 (mean: 1.78). The amount of free and total chlorine detected in the swimming pool in this study has higher values and a wider range than those in the study by Zhang et al. (2015). This is a major disadvantage of applying chlorine by manual application. The UV_{254} values in the pool water examined here were also quite high in comparison to those reported by Zhang et al. (2015). This implies a higher level of precursors introduced

Table 3. Parameters, devices and methods.

Parameter	Device	Method
TOC	Teledyn Tecmar Torch TOC/TN Analyzer	Standard Methods 5310-B
TN		Standard Methods 4500N-B
pH/temperature	Hach Hq40d Multimeter	USEPA Electrode Method 8156
Conductivity		USEPA Direct Measurement Method 8160
ORP		Direct Measurement Method 10228
HAA_s	Agilent 7890 GC-μECD	USEPA Method 552.3
THMs HANs CH CP (Chloropicrin) 1,1-DCP 1,1,1- TCP		USEPA Method 551.1
Free chlorine	Lovibond Comparator	Standard Methods 4500 Cl-G
Total chlorine		
NO_3^--N (Nitrate)	WTW Photolab 7600 model UV Vis Spectrophotometer	Standard Methods 4500 NO_3^-- B
Br^- (Bromide)		Standard Methods 4500 Br-B
UV_{254}		Standard Methods 5910-B
Alkalinity	–	Standard Methods 2320-B
Hardness	–	Standard Methods 2340-C
Turbidity	WTW Turb 355 IR	ISO 7027 – DIN/EN 27 027
AOX	Analytik Jena Multi X2500	BS EN ISO 9562:2004

Table 4. Results of pool water and groundwater quality analyses during the monitoring period.

			Pool water			
Parameter	Unit	Groundwater	Mean	Min	Max	Std Dev.
TOC	mg/L	0.30	2.48	0.92	3.89	0.73
TN	mgN/L	2.68	5.82	2.21	6.84	1.18
pH	–	7.38	8.16	7.37	8.67	0.33
Conductivity	μS/cm	277	540	489	603	34.09
ORP	mV	187.1	444.2	174.6	570.2	112.54
Temperature	°C	21.4	26.3	24.8	27.6	0.79
Free chlorine	mg/L	0	0.8	0	2.2	0.68
Total chlorine	mg/L	0	1.4	0	2.8	0.77
Combined chlorine	mg/L	0	0.6	0	1.2	0.30
NO_3^-	$mgNO_3^-/L$	3.2	6.3	3.1	9	1.43
Br^-	mg/L	0.23	1.59	0.16	3.44	1.09
Swimmers	People/day	–	88	44	202	36.95
Turbidity	NTU	0.440	0.293	0.015	0.853	0.22
UV_{254}	1/cm	0.003	0.036	0.017	0.057	0.01
Alkalinity	$mgCaCO_3/L$	124	–	–	–	–
Hardness	$mgCaCO_3/L$	200	–	–	–	–

into the pool by swimmers. The nitrate value in the pool was very low in comparison to indoor pools in China. The pH values were approximately the same.

The concentration of bromide detected in pool water can reach up to 15-fold the value in groundwater. This indicates that bromine accumulates due to circulation of the pool water without replacement or introduction of chemicals. This provides the basis for formation of brominated DBPs which are more carcinogenic than chlorinated species. Precursors and chlorine introduced to the water significantly increases the conductivity and oxidizability values of the water. The values of the parameters that were examined in this study are in parallel to those found by Ilyas et al. (2018) and higher in pool water than groundwater. This shows that precursors from swimmers significantly change pool water quality.

Groundwater hardness level was classified as very hard water (> 181 $mgCaCO_3/L$) according to USGS scale. Typical surface waters have low hardness and low alkalinity (hardness: 90 mg/L and alkalinity: 100 mg/L as $CaCO_3$). Typical groundwater has hardness and alkalinity concentrations of 120 and 150 mg/L, respectively. In this context, the groundwater examined in this research had low alkalinity and high hardness. According to the literature, higher alkalinity produces lower THMs. Also waters with high pH (pH = 10) and high hardness (160 mg/L) produce lower THMs (David 2014).

The results of the THM measurements performed in the pool water in the study are given in Figure 2. The THM_4 concentrations obtained in the study varied between 30.8 and 158 µg/L, and the mean THM_4 concentration was 85.4 µg/L. Bromoform was the most significant THM component, and the mean value for the monitoring period was 70.2 µg/L. Bromoform concentration in the pool could reach up to 131 µg/L. This is the result of an incremental increase in the concentration of bromide in the pool water. When the values that were obtained were compared to those in Table 2, the THM_4 concentrations were higher than those obtained in other countries with the exception of the mean values obtained in the UK and Canada. The bromoform value was higher than the THM_4 value obtained in most countries.

The change in HANs in the pool water in the monitoring period is shown in Figure 3.

The concentrations of HANs during the monitoring period ranged from 0.04 to 6.85 µg/L with a mean concentration of 3.52 µg/L. Bromochloroacetonitrile (BCAN) and trichloroacetonitrile (TCAN) species were not found in pool water. The most significant type of HAN was dichloroacetonitrile (DCAN), similar to Zhang et al. (2015), and it constituted 95% of HANs. The mean concentration value was very close to the one obtained in China as shown in Table 2. HAN production needs nitrogenous compounds in

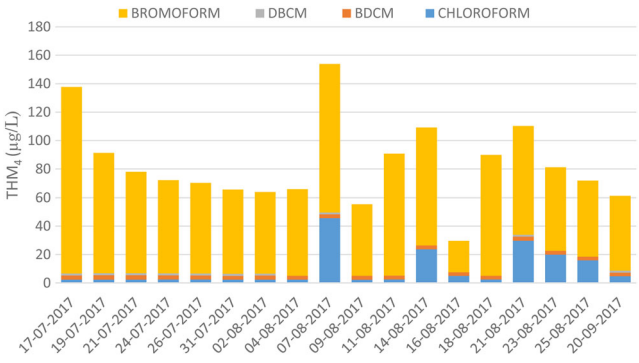

Figure 2. THM results in the monitoring period.

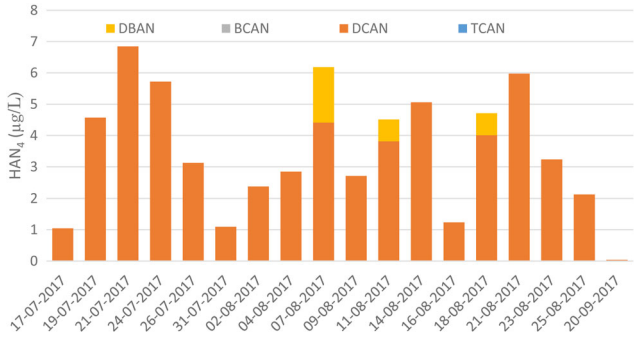

Figure 3. HAN results in the monitoring period.

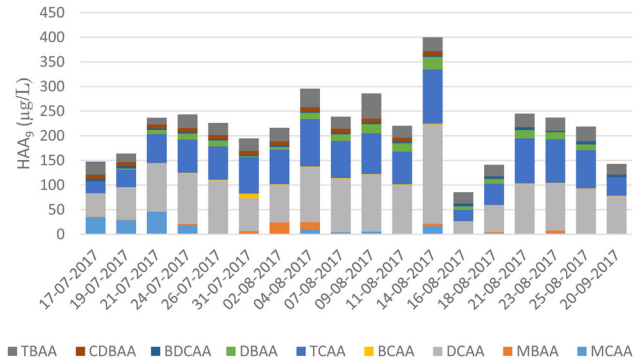

Figure 4. HAA_9 results in the monitoring period.

addition to organics. In this study nitrogenous compounds were low and this limited HAN production (Lee et al., 2010)

The HAA_9 test results for the monitoring period are given in Figure 4.

HAA_5 and HAA_9 concentrations varied between 57 and 359 µg/L and between 85.7 and 400 µg/L, respectively. The mean HAA_5 and HAA_9 concentrations found in the measurements were 181 and 219 µg/L, respectively. DCAA and TCAA were the most significant types of HAAs.

When HAA_9 values gathered here are compared to the literature values given in Table 2, it is observed that they were higher than the values obtained in Italy but lower than those in other countries. The results

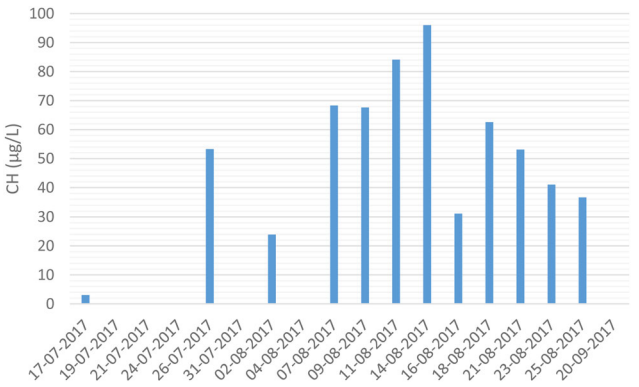

Figure 5. Chloral hydrate results in the monitoring period.

are in parallel with those reported in the literature, and HAAs were found to be the most common group among the DBPs in the pool water followed by THMs. Significant differences between the concentrations of HAA_9 and HAA_5 levels were due to the fact that high amounts of bromide in the pool water led to high amounts of brominated HAA species.

The change in CH concentration in the pool water is shown in Figure 5. CH was not detected on 6 of the 18 days monitored. The maximum concentration detected in the pool was 96 µg/L, and the mean concentration was 34.5 µg/L. Although the mean concentration was close to those in the literature as shown in Table 2, the range varied significantly.

Among the other components measured in the study, 1,1-DCP was only detected on 19.07.2017 at 1.2 µg/L and could not be detected on other days. 1,1,1-TCP was not detected in pool water during the measurement period. The measurement period mean values of these two components were below the values specified in Table 2.

In order to characterize all types of DBPs as result of water chlorination during the monitoring period, AOX parameter was also measured, and the amount of measured DBPs as a proportion of AOX in the water was determined (Avsar et al., 2014, 2015). From this, the amounts of organic halogenated compounds which cannot be measured in water were estimated. The distribution of AOX and the AOX measurement results are given in Figure 6.

Figure 6 indicates that HAAs constitute 26.2% of AOX, while THMs constitute 16.2%. CH correspond to 3.7% of the AOX, whereas HANs constitute 0.4%. The ratios of other halogenated organic compounds in AOX in the measurement period vary between 18.3% and 83.8%. AOX had a minimum of 18% and a mean value of 53.5% among other halogenated organic compounds which could not be determined on a species

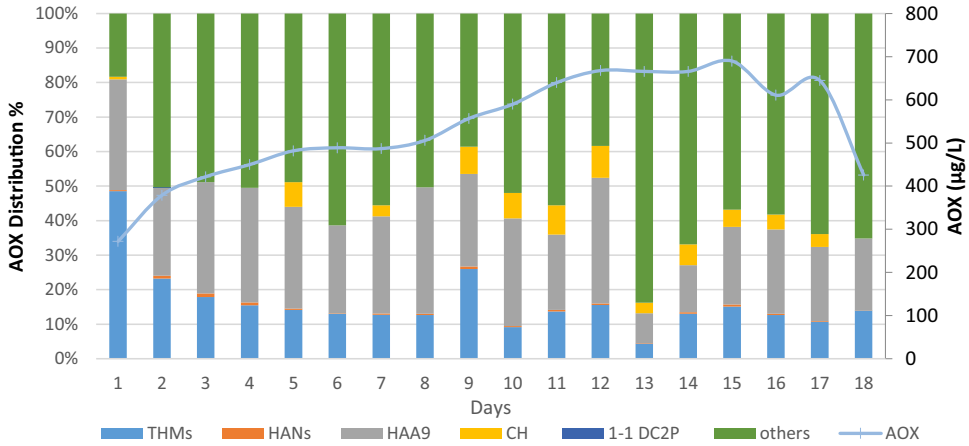

Figure 6. AOX distribution in the monitoring period.

basis. This situation creates uncertainty in terms of health hazards that may arise and is an issue that needs to be investigated.

Avsar and Toroz (2018) conducted a study to determine the potential of DBP formation as a result of chlorination in Istanbul Büyükçekmece (BC) and Ömerli (OM) raw water resources and monitored DBP parameters which were the same as the ones estimated in our study. When the mean values of both water resources in their study are considered, THMs (BC: 20.4%; OM: 21%) and HAAs (BC: 18.2%; OM: 17.3%) were determined to be the most important components of AOX. The mean contribution of other undetected halogenated organic compounds to AOX was determined to be 59.4% in OM and 58% in BC. It was observed that compounds that cannot be detected on a species basis were the most important part of AOX in both water bodies when raw water was compared to pool water. According to the results, AOX production increased along with increased TOC and TN.

4.2. Relationship between water quality parameters and DBP formation

Table 5 shows the Pearson correlations between the quality parameters and DBPs production in the pool for the monitored period.

There were significant positive correlations between AOX formation in the pool water and the TOC, TN, conductivity, total chlorine and nitrate parameters and a significant negative correlation between AOX formation and temperature. This shows that formation of halogenated organic compounds in the water was influenced by the precursor amounts in the water and the physical conditions in the pool. These parameters are the fingerprint of DBP formation in the pool water. Positive or negative changes in these parameters directly affect DBP formation. In contrast to Zhang et al. (2015), significant correlations were found between the TOC parameter and HAA_9, HANs and CH formation. There was also a positive correlation between formation of these DBPs and combined chlorine. However, similar to the results reported by Zhang et al. (2015), no significant correlation was detected between THMs and any other parameter. As described by Zhang et al. (2015), no significant correlation was found between UV_{254} and DBP formation. Since the precursors from swimmers had low aromaticity, UV_{254} did not serve as an indicator in pool water.

4.3. Risk analysis

In the second stage of the study, the health risks of swimmers who use the swimming pool and are exposed to DBPs formed after chlorination were evaluated. A methodology previously described in the literature was utilized for this purpose (Gan et al., 2013). Estimations were performed for four THM (Chloroform, Bromodichloromethane (BDCM), Dibromochloromethane (DBCM), and Bromoform) and two HAA (Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA)) species. Estimations for HANs and other DBPs were not implemented as there is no report about the necessary constants in the literature.

4.3.1. Risk assessment for THMs

Cancer risk analysis for THM was performed for the two means of exposure, ingestion and dermal absorption. Risk analysis for HAA could only be applied for ingestion (Gan et al., 2013; Avsar, 2018; Kilic, 2018).

4.3.1.1. Risk of Ingestion. The risk of ingestion was calculated according to the method described by Gan

Table 5. Pearson correlations between the parameters monitored in the pool.

	TOC	TN	Conductivity	ORP	Temperature	Free Cl_2	Total Cl_2	Combined Cl_2	NO_3^-	Br^-	Swimmers	CH
TN	0.670**											
Conductivity		0.569*										
ORP												
Temperature		−0.588*	−0.947**									
Free Cl_2				0.797**								
Total Cl_2				0.850**		0.924**						
Combined Cl_2	0.735**	0.564*					0.485*					
NO_3^-			0.632**		−0.690**	0.632**	0.600**					
Br^-				0.789**		0.905**	0.868**		0.715**			
Swimmers		−0.512*										
Turbidity					−0.476*	0.611**	0.600**		0.601**	0.512*		
HAA_9	0.469*							0.549*				
THM_S												
HAN_S	0.491*						0.486*	0.615**				
CH	0.600**							0.497*				
1-1 DC2P		−0.743**									0.757**	
AOX	0.637**	0.603**	0.689**		−0.627**		0.469*		0.506*			0.739**

Notes: ** $P < 0.01$.
*$P < 0.05$.

Table 6. Ingestion-based risk calculations of THMs for women.

Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	3.0×10^{-9}	3.3×10^{-8}	2.4×10^{-8}	3.7×10^{-8}	9.7×10^{-8}
Maximum	5.9×10^{-8}	4.0×10^{-9}	1.9×10^{-9}	2.2×10^{-7}	2.9×10^{-7}
Mean	1.2×10^{-8}	3.6×10^{-9}	1.8×10^{-9}	1.2×10^{-7}	1.4×10^{-7}

Table 7. Ingestion-based risk calculations of THMs for men.

Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	2.7×10^{-9}	2.9×10^{-8}	2.1×10^{-8}	3.3×10^{-8}	8.6×10^{-8}
Maximum	5.2×10^{-8}	3.6×10^{-8}	2.3×10^{-8}	1.9×10^{-7}	3.1×10^{-7}
Mean	1.1×10^{-8}	3.2×10^{-8}	2.2×10^{-8}	1.0×10^{-7}	1.7×10^{-7}

Table 8. Dermal exposure-based risk calculations of THMs in men.

Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	4.2×10^{-12}	2.9×10^{-11}	1.5×10^{-11}	1.5×10^{-11}	6.3×10^{-11}
Maximum	8.2×10^{-11}	3.7×10^{-11}	1.6×10^{-11}	8.9×10^{-11}	2.2×10^{-10}
Mean	1.7×10^{-11}	3.3×10^{-11}	1.5×10^{-11}	4.8×10^{-11}	1.1×10^{-10}

Table 9. Dermal exposure-based risk calculations of THMs in women.

Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	4.4×10^{-12}	3.1×10^{-11}	1.6×10^{-11}	1.6×10^{-11}	6.7×10^{-11}
Maximum	8.6×10^{-11}	3.9×10^{-11}	1.7×10^{-11}	9.4×10^{-11}	2.4×10^{-10}
Mean	1.8×10^{-11}	3.5×10^{-11}	1.6×10^{-11}	5.0×10^{-11}	1.2×10^{-10}

Table 10. Ingestion-based risk calculations of HAA for women.

Risk	DCAA	TCAA	Total
Minimum	2.5×10^{-7}	3.0×10^{-7}	5.5×10^{-7}
Maximum	1.9×10^{-6}	1.4×10^{-6}	3.3×10^{-6}
Mean	8.6×10^{-7}	8.7×10^{-7}	1.7×10^{-6}

et al. (2013) with the aid of constants given in studies by Avsar (2018) and Kilic (2018) and the minimum, maximum and mean concentrations of DBP species. Detailed calculations are given in the supplementary materials file. The ingestion-based risk calculations for women are given in Table 6, and those for men are given in Table 7.

According to the EPA, if the probability of occurrence of any event exceeds one in a million, the minimum or negligible risk level for that event has been exceeded (Gan et al., 2013). When the values obtained in this context are analyzed, it is observed that ingestion of the pool water did not constitute a great risk for women or men under the specified conditions.

4.3.1.2. Dermal exposure risks.

Exposure to THMs through dermal absorption was calculated in an analogous manner (Gan et al., 2013; Avsar, 2018; Kilic, 2018). Dermal exposure-based risk calculations for men and women are given in Tables 8 and 9.

The results of the analyses revealed that swimming pool usage under the specified conditions did not pose a risk for women or men based on the "one-in-a-million" rule.

4.3.2. Risk assessment for HAAs

4.3.2.1. Risk of ingestion.

The risk of HAAs ingestion was estimated similarly to the risk assessment process for THMs (Gan et al., 2013; Avsar, 2018; Kilic, 2018). Detailed calculations are given in the supplementary materials file. The ingestion-based risk calculations of HAAs for women are given in Table 10, and those for men are given in Table 11.

When the estimated risk values of HAA for both men and women are examined, it is observed that, at the maximum concentration, the risk thresholds for the sum of both pollutants were exceeded. It should not be forgotten that when THMs, HAAs and other DBPs in the pool water are considered together, the risk increases even more.

Table 11. Ingestion-based risk calculations of HAA for men.

Risk	DCAA	TCAA	Total
Minimum	2.9×10^{-7}	3.4×10^{-7}	6.3×10^{-7}
Maximum	2.1×10^{-6}	1.6×10^{-6}	3.8×10^{-6}
Mean	9.8×10^{-7}	9.9×10^{-7}	2.0×10^{-6}

5. Conclusion and recommendations

The study provides fingerprinting information for DBPs formed under uncontrolled water quality conditions; it may also suggest the compounds to be expected based on pool water composition. In this study, pool water quality and DBPs were monitored in the summer of 2017 in a swimming pool in the province of Bitlis in Turkey. The study led to the following conclusions;

The free chlorine level in the pool water was very variable because of manual chlorination, and most of the time, it was below the required level.

Due to the fact that the swimming pool water was filtered using a closed circuit system which removes only suspended solids, the TOC and TN compounds that dissolved in water increased over time, and the increase in the UV value in parallel to these increased the potential for DBP formation in the water.

The mean values of THMs that formed in the water were higher than those reported in many studies in the literature. Similar to the literature, the amount of HAA was higher than the amount of THM. An increase in brominated HAA species was observed in parallel with the increase in the amount of bromide in the water. This situation was attributed to filtering of water with a closed-circuit system which causes bromide to accumulate in water. This leads to formation of more carcinogenic brominated DBPs in addition to chlorinated by-products.

The compounds that cannot be identified on a species basis constituted a large portion of AOX formed in the pool. Significant positive correlations between AOX formation in the pool water and the TOC, TN, conductivity, total chlorine and nitrate parameters and a significant negative correlation between AOX formation and temperature were observed. Since the precursors from swimmers had low aromaticity, UV_{254} did not have the potential to serve as an indicator in the pool water.

In the context of the risk assessment process, the values calculated for HAAs were found to have the potential to pose a risk to public health. In this context, stable chlorination conditions should be provided in the pool. It is concluded that the chlorine level in the pool exceeded the required level in both directions due to the fact that chlorination was implemented manually, and thus, no uniform chlorination was performed. As a result of excess chlorination of water, chlorine reacts with the precursor compounds in the water significantly and causes a high amount of DBP formation in comparison to the levels reported in the literature.

In order to prevent accumulation of nitrogenous and carbonaceous precursor compounds, swimmers should be required to take a shower before entering the pool. Moreover, use of foot disinfection pools that are available at the pool entrance but were not actively used at the time must be enforced. This system that was originally designed to prevent cross contamination of microorganisms and fungi through feet is a very crucial component. Chemicals specifically developed for such pools are available, and they must be supplied and used.

The pool management stated that the pool was filled at the beginning of the summer season and continuously used until the end of the season. Therefore, it is recommended that the water should be emptied at least once a month during the swimming season and replaced regularly and more frequently to reduce accumulation of precursor compounds in the pool.

The aforementioned measures are aimed at reducing formation of DBPs, and it is recommended to re-examine the amounts of DBPs formed in the pool after implementation of these measures. In the case of detection of high amounts of DBPs, sand filters and active carbon filters may be used to reduce the amounts of these DBPs. Instead of chlorination, alternative disinfection methods such as UV, ozone or chlorine dioxide disinfection may be tested. Implementation of such studies and evaluation of the results would be an interesting research topic.

In this integrated case study, uncontrolled conditions (pH, manual chlorination, chlorine dose, temperature, bromine concentration, TOC, TN) negatively affect the DBPs level and dramatically increase the concentration in water. Therefore these parameters are the fingerprint of DBP formation in the studied pool water. Positive or negative changes in these parameters directly affect DBP formation.

Acknowledgements

This manuscript was written by the contribution of all authors. The authors wish to thank Bitlis Sports High School that assisted in conducting this work.

Funding

We would like to sincerely thank Bitlis Eren University Scientific Research Projects Division (Project No: BEBAP 2017-18) for supporting this study.

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