Al-Quds Journal for
Academic Research

The Occurrence of Disinfection By-Products (DBPs) in Chlorinated Recreational Water, Palestine

RESEARCH

Amer Kanan[1,*] and Mohannad Qurie[1]

[1] Department Environment and Earth Sciences, College of Science & Technology, Al-Quds University, Jerusalem, Palestine.

ABSTRACT

Recreational water disinfection is an essential treatment for controlling microbial activity. However, chemical disinfectants are powerful oxidants that react with the natural organic matter, anthropogenic contaminants, and bromide present in water and produce unintended disinfection by-products. Chlorine is the most used water disinfectant in Palestine. In this study, water samples from 9 swimming pools present in 3 Governments in the West Bank in Palestine were analyzed to investigate the occurrence of trihalomethanes which are the main and most reported disinfection by-products formed in chlorinated waters. Results show that these pools are poorly managed and do not comply with recommended guidelines for recreational water quality. The pH of some of the water-monitored swimming pools did not comply with the pH guideline for swimming pools. The free chlorine residual measured in the swimming pools' water was higher than recommended values or much less than required. DBPs in the form of THMs measured in the samples from the pools were in the range 386 to 2856 ppb. These amounts of DBPs exceed what has been reported in the recreational water in other countries and are far away from recommended levels. Brominated THMs that impose higher toxicity compared to chlorinated analogs were detected in all 9 swimming pool samples. The bromine substitution factor for all samples was calculated and showed a correlation with the pH of the water sample.

Keywords: Recreational water; Swimming pools; Chlorination; Disinfection Byproducts; Trihalomethanes.

Introduction

Disinfection of water using chlorine is a common practice in Palestine. Chlorine is widely used in water disinfection because it is effective and inexpensive. The disinfection as chlorine is applied to water to deactivate microorganisms and ensure residual concentration to prevent microorganisms' regrowth (Chowdhury et al., 2014; Tang 2020). The presence of disinfection by-products (DBPs) in chlorinated water was first reported in the 1970s (Bellar et al., 1974; Rook, 1976; Symons et al., 1975). Chlorine reacts with natural organic compounds, and human body excretes contained in pool water producing hundreds of DBPs (Kanan and Karanfil, 2011; Wigle, 1998). In recent years, special interest has been developed with regard to the occurrence of DBPs in chlorinated recreational water. More attention has been paid to the concentration of trihalomethanes (THMs), which are the most commonly occurring group of DBPs (Manasfi et al., 2017; Weaver et al., 2009; Zwiener et al., 2007). THMs have been studied due to their high concentrations, frequency of occurrence, and possible toxicity (Aggazzotti et al., 1998; Kanan and Karanfil, 2011; World Health Organization, 2006). The four main species of THMs that form as a result of water chlorination are: chloroform ($CHCl_3$),bromodichloromethane($CHC_{l2}Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$) (Golfinopoulos, 2000; Kanan et al., 2015). The main operational and water quality parameters that influence the formation of THMs are chlorine dose, organic matter in pool water (both natural and anthropogenic), water temperature, pH, and contact time (Kanan et al., 2015). Moreover, bromide,

Dr Amer Kanan passed a way beofre the publication of this article, may his Soul rest in Peace. Condolences to his family, students and colleagues.

Correspondance:
Department of Environment & Earth Sciences, Al-Quds University, Abu Dies, P.O.Box P.O.Box 20002 Jerusalem, Palestine.
E-mail: akanan@staff.alquds.edu / mqurie@staff.alquds.edu

which is present in filling water from either natural or anthropogenic sources, has an important effect on THMs speciation (Kanan et al., 2015; Stuart et al., 2001). Swimming pool water has both natural organic matter, coming with filling water, and human body excretions that swimmers release. Both types of organics are considered and proved to be DBPs precursors (Kanan and Karanfil, 2011; Keuten et al., 2014). Epidemiological studies have suggested that THMs are potentially carcinogenic (World Health Organization, 2006). Furthermore, an association between exposure to THMs and spontaneous abortion, growth retardation, and birth effects has been reported (Plewa et al., 2004; Wigle, 1998). The pool water, if not filtrated and disinfected continuously, becomes a severe health risk to the swimmers. According to the WHO, there are three main routes of exposure to chemicals in swimming pools: inhalation, dermal contact, and direct ingestion (World Health Organization, 2006).

Swimming pools of all types should be maintained in satisfactory physical, chemical, and biological conditions (World Health Organization, 2006). The DBPs that have been detected in swimming pools vary with the disinfectant used (Chowdhury et al., 2014; Fantuzzi et al., 2001; World Health Organization, 2006). Although residual disinfectant levels must be maintained to ensure disinfection, the optimization of disinfectant concentration and the proper time and method of disinfection used must be regulated because disinfectants themselves are harmful and have been reported to have adverse health effects, too (World Health Organization, 2006). The level of recommended chlorine residual in swimming pool water varies from country to country: UK 1-2 mg/L, USA 1-3 mg/L, Germany 0.3-0.6 mg/L and Italy 0.6-1.2 mg/L (Kanan, 2010; Kanan et al., 2015; World Health Organization, 2006).

In Palestine, the number of swimming pools has increased recently. There are several private, semi-public (hotel, health club) and public pools, both indoor and outdoor pools in Palestine. The source of water used in filling the swimming pools is municipal groundwater. Chlorine, in its different forms (Sodium hypochlorite and Calcium hypochlorite), is the main disinfectant used in the swimming pools (Al-Khatib and Salah, 2003). DBPs that are produced as a result of pool disinfection should be at levels that are at least comparable to those produced in drinking water disinfection. In Germany and Switzerland, THMs levels in swimming pools should not exceed 20 ppb as $CHCl_3$. In Denmark 50 ppb as $CHCl_3$ is the limit (Borgmann-Strahsen, 2003; Kanan et al., 2015). The National French Institute of Research and Security recommends a maximum of 0.5 mg/m^3 in the air around a swimming pool (Barbot and Moulin, 2008). However, DBPs found in pool waters easily exceed these levels due to water recycling in swimming pools, the continuous addition of organic precursors by bathers and water replenishment, and continuous chlorination (Fantuzzi et al., 2001; Kanan, 2010; Zhao et al., 2004). Regular swimmer's blood plasma chloroform is highly elevated after a swimming event (Aggazzotti et al., 1998). Swimming pools should be properly managed to meet the recommended water disinfection standards or maintain other chemical, biological, and physical water properties (Al-Khatib and Salah, 2003; Chowdhury et al., 2014; Kanan, 2010; Khatib and Ghannam, 2011, Huang, 2020).

In this study, we report the occurrence of the main DBPs (THMs) in chlorinated recreation water sampled from 9 swimming pools in Palestine and the operational characteristics of the swimming water samples. Bromide substitution factor was calculated for THMs measured in swimming pool water samples.

Materials and methods

Sampling

To investigate the occurrence of THMs in the recreation water of the swimming pools, water samples were collected from 9 swimming pools from 3 different governorates in the West Bank, Palestine, in summer 2018. Samples for THM measurements were collected in 60 mL glass amber-brown vials with Teflon lined screw caps from Supelco. Water samples were collected 30 cm below the swimming pool water surface using a manual pump by immersing a pipe underwater. The vials were filled carefully just to overflowing capacity, without passing air bubbles through the sample or trapping air bubbles in sealed vials. Ascorbic acid, a quenching material, was added (10 mg for 10 mL sample) to the water samples at the end of each specific incubation period to prevent further THMs formation. Free chlorine residual (FAC), pH, and water temperature of samples were measured on-site using pH-EC-TDS portable meter HI 9812 from HANNA, while FAC was measured using HACH 2010 spectrophotometer.

The chemical and reagent used in the experiments, hypochlorite reagent: 100 mL of NaOH 1N was added to 100 mL of D.W, then 6 mL of 11% sodium hypochlorite was added (catalog No. 48481) and mixed very well; the total volume should be 206 mL. Finally, the reagent was stored in dark bottles for only two weeks. Standards prepared from ammonia stock solution of 1000 mg/L. DPD Free Chlorine Powder Pillows (catalog number 21055-69). Sodium hydroxide and Phosphate buffer were used to maintain pH during the THMFP test. Ascorbic acid was used as a quenching reagent to stop chlorine reaction before THM analysis.

THMs analysis

The headspace method, which is suitable for samples with high contents of THMs, was used. It has the advantage of being rapid with good replication and minimal solvent handling and waste production (Cho et al., 2003; Nikolaou et al., 2002). In addition, it has an acceptable detection limit without contamination risk from the solvent (Barbot and Moulin, 2008; Kuivinen and Johnsson, 1999; Nikolaou et al., 2002; Stack et al., 2000). From each sample, 5 mL of water were transferred into a 10 mL headspace vial. The vial was sealed with stainless steel crimp top cap equipped with PTFE-lined septa. The vials were statically incubated at 95 °C for 20 minutes in a CombiPal autosampler (CTC Analytics AG, Switzerland). 1000 µL of the headspace was subsequently withdrawn and injected into a 6890N Agilent GC/MS injector at 300 µL/s. The separation was performed using the J&W-VRX column. The oven temperature was held at 40 °C for 4 min, ramped to 45 °C at 0.5 °C/min, held for 2 min, ramped to 70 °C at 2.0 °C/min, and ramped to 150 °C at 10 °C/min. The injections were done in split mode (split ratio 2.0), with injector temperature at 220 °C, transfer line temperature at 280 °C, and ion source temperature at 230 °C. SIM method was developed for the different THMs species (Chloroform, Bromodichlo romethane,Dibromochloromethane,Bromoform) following USEPA method No. 501. External standard calibration was used to obtain calibration curves in the concentration range from 10 to 300 µg/L for each species. Standards were prepared from a standard stock solution (Supelco Cat. No 48746). Water samples were subjected to appropriate dilution prior to measurement so that measured values were in the range of calibration.

Results and discussion

Water characteristics

Physiochemical properties of the water samples from the studied swimming pools are presented in Table 1. To obtain the maximum disinfection effect, the pH of the water in a swimming pool must be in the range of 6.5-7.6; chlorine efficiency in inactivating pathogens decreases at pH 8 and above (World Health Organization, 2006). The pH of some of the swimming pools water investigated did not comply with this pH guideline. The free chlorine residual (FAC) measured in the water samples from the studied pools did not achieve the recommended values in many of the pools studied. The free chlorine residual in the water of swimming pools that the United Kingdom recommends is 1-2 mg/L and 1-3 mg/L by American National Standard Institute (World Health Organization, 2006).

Table 1. Physiochemical properties (operational parameters) of water samples were collected from 9 swimming pools from 3 different governorates in the West Bank, Palestine

Pool	pH	Temp (ºC)	FAC* (mg/L)
Pool 1	8.2±0.1	26.2±0.1	0.1±0.1
Pool 2	7.2±0.1	26.8±0.1	1.8±0.1
Pool 3	6.8±0.1	29.1±0.1	0.6±0.1
Pool 4	7.7±0.1	28.3±0.1	1.6±0.1
Pool 5	7.4±0.1	29.2±0.1	2.2±0.1
Pool 6	7.8±0.1	29.1±0.1	1.1±0.1
Pool 7	7.7±0.1	25.2±0.1	0.9±0.1
Pool 8	7.4±0.1	24.6±0.1	0.9±0.1
Pool 9	7.3±0.1	23.5±0.1	0.9±0.1

** FAC: Free Available Chlorine*

One of the pools of water had a very low free chlorine residual (0.1 mg/L) that had the highest pH (8.2). This low free chlorine residual results from the low dissociation rate of chlorine disinfectant due to the high pH and/or low dose of chlorination. Chlorine equilibrium in water between hypochlorous acid (HOCl) and hypochlorite (OCl^-) is a function of temperature and pH (Hansen et al., 2013). The efficiency of hypochlorous acid in disinfection is more than hypochlorite, and this implies that a swimming pool pH monitoring and control is decisive for pool water disinfection effectiveness.

THMs occurrence in recreational water

Four THMs species were quantified in each pool water sample. In all samples, total THMs were very high compared to their occurrence in drinking water or relative to regulations of different countries that regulate THMs in swimming pools (Figure 1).

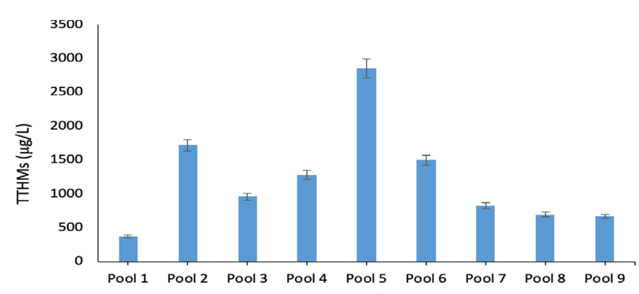


Figure 1. The occurrence of TTHMs in 9 swimming pools samples collected from three different governorates in the West Bank, Palestine.

Chloroform is the most abundant trihalomethane, and bromoform is the minor trihalomethane measured in 8 swimming pools (Figure 2). However, in one pool (pool 1), the brominated trihalomethane species were the prominent forms of THMs. Brominated species result from Br- presence in the swimming pool water that comes from the filling groundwater. Bromide is ubiquitous in all fresh waters in the range of few µg/L to several mg/L (Magazinovic et al., 2004) depending on geological situations and sea intrusion in coastal areas, which are responsible for the observed high bromide levels in addition to anthropogenic activities (Heeb et al., 2014). Bromine in the form HOBr or BrO-, is formed when bromide is in the water background due to the oxidation of Br- by chlorine. When bromine is formed, it can react with organic matter leading to the formation of brominated THMs (Tan et al., 2016). These brominated species are more toxic than their chlorinated analogs (Plewa et al., 2004)

The maximum total trihalomethane, which was measured in pool 5 is 2856 ppb and the minimum, which was measured at pool 1 is 368 ppb. These values are significantly high compared to what has been reported in swimming pools waters in different countries (Kanan, 2010).

The ranges reported by the WHO for different countries are lower than 500 ppb in most cases (World Health Organization, 2006).

The chloroform concentrations measured in other studies in swimming pool waters mean values are from 14 to 198 ppb, and other trihalomethanes were lower (Fantuzzi et al., 2001; Kanan, 2010). Considering this, better and careful management and monitoring of swimming pools are required in Palestine to make the water of swimming pools safer and minimize the possible adverse health impacts on the swimmers.

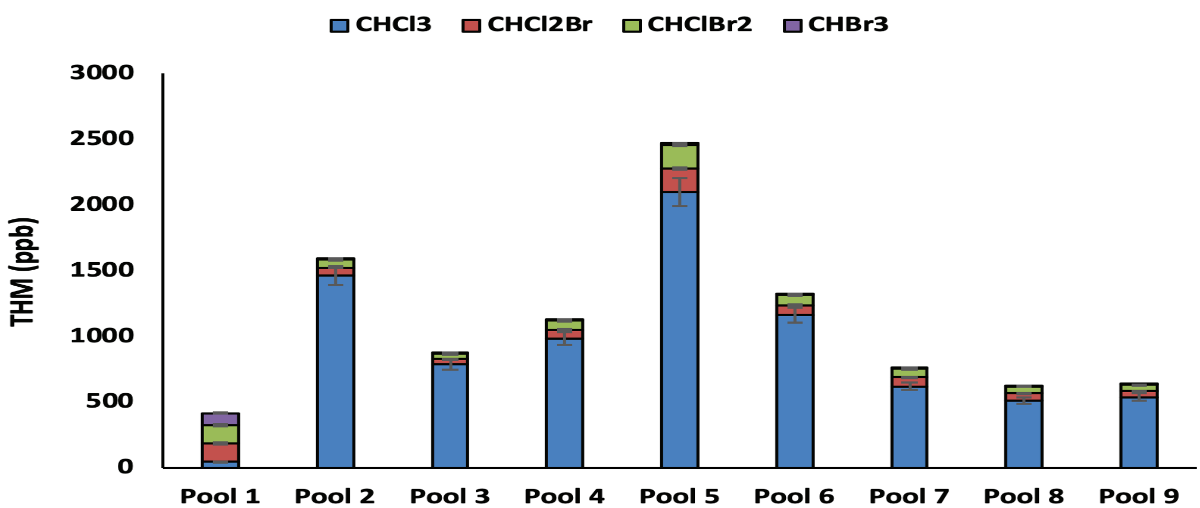
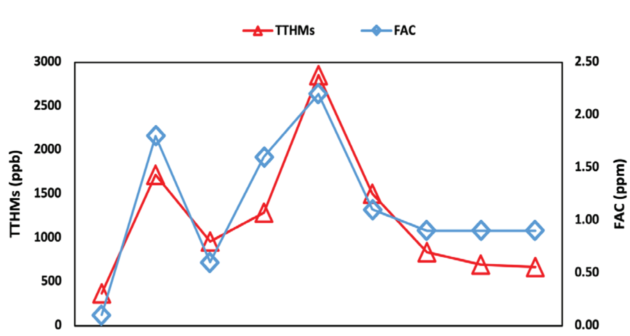


Figure 2. THMs speciation in samples from swimming pools in Palestine. Chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), bromoform ($CHBr_3$).

FAC effect on THMs formation

The proportionality of free chlorine and trihalomethane formation is obvious through the increasing of THMs by increasing the free chlorine residual (Figure 3).



Bromine substitution

To evaluate the bromine substitution during DBPs formation and speciation, the bromine substitution factor (BSF) index (Hua and Reckhow, 2012) is used to investigate the substitution level of bromine in THMs. More bromine incorporation is noticed when higher bromide to chlorine ratios are present in water. The BSF is the percentage of bromine in the total halogen of each class of DBP (in micromole), and it can vary from 0 to 1, as shown in equation (1) (Hua and Reckhow, 2012).

Figure 3. The relation between free available chlorine (FAC) and THMs concentration. The lines are to guide the eye.

$$BSF = \frac{DBP - Br}{DBP - (Cl + Br)}$$

This equation for THMs can be written as follow

$$SF\ (THM) = \frac{CHBrCl_2 + 2(CHBr_2\,Cl) + 3(CHBr_3)}{3(CHCl_3 + CHBrCl_2 + CHBr_2Cl + CHBr_3)}$$

The BSF index can be used as an unbiased measure of bromine substitution among different DBP species and classes. Figure 4 presents the BSF (as percent %) of THMs in swimming pools investigated in this study as a function of water pH, which is a disinfection condition that can affect the DBPs formation and impact the competition between chlorine and bromine in substituting when reacting with organic matter(Obolensky and Singer, 2005).

The BSF index can be used as an unbiased measure of bromine substitution among different DBP species and classes. Figure 4 presents the BSF (as percent %) of THMs in swimming pools investigated in this study as a function of water pH, which is a disinfection condition that can affect the DBPs formation and impact the competition between chlorine and bromine in substituting when reacting with organic matter (Obolensky and Singer, 2005). As shown in Figure 4, bromine substitution increased as the swimming pool water pH increased, implying more toxicity (Ersan et al., 2019; Plewa et al., 2004) of DBPs in swimming pool water.

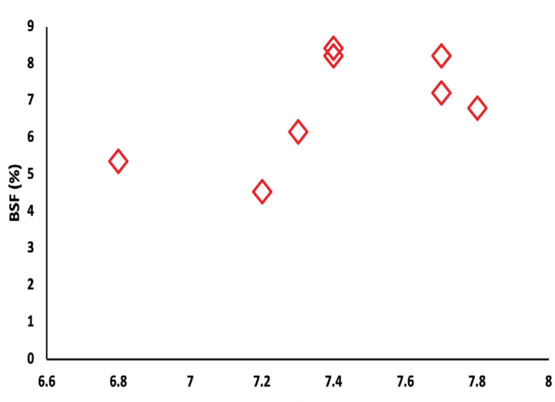


Figure 4. Bromine substitution factor (BSF %) as a function of pH in swimming pool water, Palestine

Conclusions

In all swimming pools sampled in this study, the total THMs measured are many folders more than the recommended amounts. Brominated analogs of THMs are present in all pools, which is an additional public health concern as brominated species are much toxic than chlorinated ones. Swimming pools in Palestine need to have special attention in terms of water quality and other operational and management aspects. Swimming pools should be safe physically, biologically, and chemically to achieve their health and sport objective.

Acknowledgments

The Authors thank Al-Quds University for providing facilities, support, and encouragement. Many thanks to colleagues from Süleyman Demirel University (SDU) (Süleyman Demirel Üniversitesi) in Isparta, Turkey for assisting in THM analysis.

Conflict of Interest

The authors declare no conflict of interest.

References

Aggazzotti, G., Fantuzzi, G., Righi, E., Predieri, G., 1998. Blood and breath analyses as biological indicators of exposure to trihalomethanes in indoor swimming pools, The Science of the Total Environment.

Al-Khatib, I.A., Salah, S., 2003. Bacteriological and chemical quality of swimming pools water in developing countries: A case study in the West Bank of Palestine. Int. J. Environ. Health Res. 13, 17–22.

Barbot, E., Moulin, P., 2008. Swimming pool water treatment by ultrafiltration-adsorption process. J. Memb. Sci. 314, 50–57.

Bellar, T.A., Lichtenberg, J.J., Kroner, R.C., 1974. The Occurrence of Organohalides in Chlorinated Drinking, Journal (American Water Works Association).

Borgmann-Strahsen, R., 2003. Comparative assessment of different biocides in swimming pool water. Int. Biodeterior. Biodegrad. 51, 291–297.

Cho, D.H., Kong, S.H., Oh, S.G., 2003. Analysis of trihalomethanes in drinking water using headspace-SPME technique with gas chromatography. Water Res. 37, 402–408.

Chowdhury, S., Al-hooshani, K., Karanfil, T., 2014. Disinfection byproducts in swimming pool: Occurrences, implications and future needs. Water Res. 53, 68–109. https://doi.org/10.1016/j.watres.2014.01.017

Ersan, M.S., Liu, C., Amy, G., Karanfil, T., 2019. The interplay between natural organic matter and bromide on bromine substitution. Sci. Total Environ. 646, 1172–1181.

Fantuzzi, G., Righi, E., Predieri, G., Ceppelli, G., Gobba, F., Aggazzotti, G., 2001. Occupational exposure to trihalomethanes in indoor swimming pools. Sci. Total Environ. 264, 257–265. https://doi.org/10.1016/S0048-9697(00)00722-1

Golfinopoulos, S.K., 2000. The occurrence of trihalomethanes in the drinking water in Greece. Chemosphere 41, 1761–1767. https://doi.org/10.1016/S0045-6535(00)00062-X

Hansen, K.M.S., Albrechtsen, H.J., Andersen, H.R., 2013. Optimal pH in chlorinated swimming pools - Balancing formation of by-products. J. Water Health 11, 465–472.

Heeb, M.B., Criquet, J., Zimmermann-Steffens, S.G., Von Gunten, U., 2014. Oxidative treatment of bromide-containing waters: Formation of bromine and its reactions with inorganic and organic compounds - A critical review. Water Res. 48, 15–42.

Hua, G., Reckhow, D.A., 2012. Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. Water Res. 46, 4208–4216.

Huang, G., Ng, T.W., Chen, H., Chow, A.T., Liu, S., Wong, P.K., 2020. Formation of assimilable organic carbon (AOC) during drinking water disinfection: a microbiological prospect of disinfection byproducts. Environ. Int. 135, 105389.

Kanan, A., 2010. Occurrence and formation of disinfection by-products in indoor swimming pools water. Clemson University.

Kanan, A., Karanfil, T., 2011. Formation of disinfection by-products in indoor swimming pool water: The contribution from filling water natural organic matter and swimmer body fluids. Water Res. 45, 926–932.

Kanan, A., Selbes, M., Karanfil, T., 2015. Occurrence and formation of disinfection by-products in indoor U.S. swimming pools. ACS Symp. Ser. 1190, 405–430.

Keuten, M.G.A., Peters, M.C.F.M., Daanen, H.A.M., de Kreuk, M.K., Rietveld, L.C., van Dijk, J.C., 2014. Quantification of continual anthropogenic pollutants released in swimming pools. Water Res. 53, 259–270. h

Khatib, I.A. Al, Ghannam, R.S., 2011. Microbiological water quality and sampling policy of public swimming pools. Int. J. Environ. Eng. 3, 192.

Kuivinen, J., Johnsson, H., 1999. Determination of trihalomethanes and some chlorinated solvents in drinking water by headspace technique with capillary column gas-chromatography. Water Res. 33, 1201–1208.

Magazinovic, R.S., Nicholson, B.C., Mulcahy, D.E., Davey, D.E., 2004. Bromide levels in natural waters: Its relationship to levels of both chloride and total dissolved solids and the implications for water treatment. Chemosphere 57, 329–335.

Manasfi, T., Temime-Roussel, B., Coulomb, B., Vassalo, L., Boudenne, J.L., 2017. Occurrence of brominated disinfection byproducts in the air and water of chlorinated seawater swimming pools. Int. J. Hyg. Environ. Health 220, 583–590.

Nikolaou, A.D., Lekkas, T.D., Golfinopoulos, S.K., Kostopoulou, M.N., 2002. Application of different analytical methods for determination of volatile chlorination by-products in drinking water, Talanta. 56:717-26

Obolensky, A., Singer, P.C., 2005. Halogen substitution patterns among disinfection byproducts in the information collection rule database. Environ. Sci. Technol. 39, 2719–2730.

Plewa, M.J., Wagner, E.D., Richardson, S.D., Thruston, A.D., Woo, Y.T., McKague, A.B., 2004. Chemical and biological characterization of newly discovered iodoacid drinking water disinfection byproducts. Environ. Sci. Technol. 38, 4713–4722.

Rook, J.J., 1976. Halforms in Drinking Water. Am. Water Work. Assoc. 68, 168–172.

Stack, M.A., Fitzgerald, G., O'Connell, S., James, K.J., 2000. Measurement of trihalomethanes in potable and recreational waters using solid phase micro extraction with gas chromatography-mass spectrometry. Chemosphere 41, 1821–1826.

Stuart, M.E., Gooddy, D.C., Kinniburgh, D.G., Klinck, B.A., 2001. Trihalomethane formation potential: A tool for detecting non-specific organic groundwater contamination. Urban Water 3, 173–184.

Symons, J.M., Bellar, T.A., Carswell, J.K., 1975. National organics reconnaissance survey for halogenated organics. J. / Am. Water Work. Assoc. 67, 634–647.

Tan, J., Allard, S., Gruchlik, Y., McDonald, S., Joll, C.A., Heitz, A., 2016. Impact of bromide on halogen incorporation into organic moieties in chlorinated drinking water treatment and distribution systems. Sci. Total Environ. 541, 1572–1580.

Tang, Y., Long, X., Wu, M., Yang, S., Gao, N., Xu, B., Dutta, S., 2020. Bibliometric Review of Research Trends on Disinfection By-Products in Drinking Water during 1975-2018. Separ. Purif. Technol. 241, 116741

Weaver, W.A., Li, J., Wen, Y., Johnston, J., Blatchley, M.R., Blatchley, E.R., 2009. Volatile disinfection by-product analysis from chlorinated indoor swimming pools. Water Res. 43, 3308–3318.

Wigle, D.T., 1998. Safe Drinking Water: A Public Health Challenge. Chronic Dis. Can. 19, 103–107.

World Health Organization, 2006. Guidelines for safe recreational water environments: Volume 2. Swimming pools and similar environments. World Heal. Organ. 2, 146.

Zhao, R.S., Lao, W.J., Xu, X.B., 2004. Headspace liquid-phase microextraction of trihalomethanes in drinking water and their gas chromatographic determination. Talanta 62, 751–756.

Zwiener, C., Richardson, S.D., DeMarini, D.M., Grummt, T., Glauner, T., Frimmel, F.H., 2007. Drowning in disinfection byproducts? Swimming pool water qualtiy. Water 34, 42–46.