

Biologically active carbon filtration for haloacetic acid removal from swimming pool water



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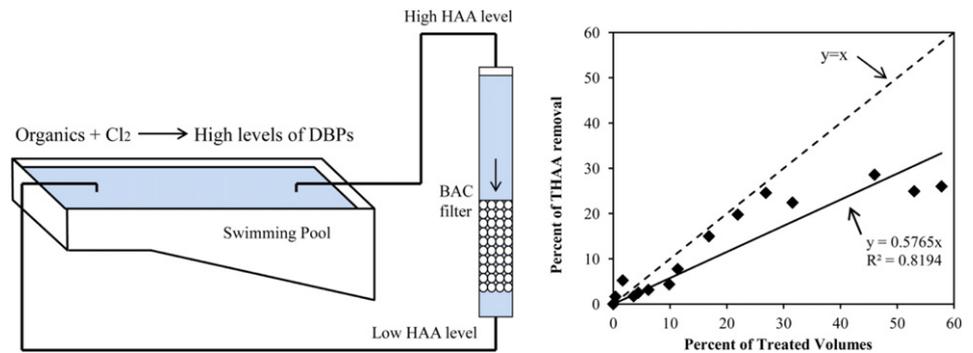
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HIGHLIGHTS

- HAA levels were reduced from chlorinated pool water by BAC filtration.
- Longer EBCT contributed to higher removal efficiency.
- BAC filtration preferentially removed DCAA over TCAA.
- Discussed the DBP formation and degradation mechanism in swimming pools

GRAPHICAL ABSTRACT



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ABSTRACT

A biologically activate carbon (BAC) filter was continuously operated on site for the treatment of haloacetic acids (HAAs) in an outdoor swimming pool at an average empty bed contact time (EBCT) of 5.8 min. Results showed that BAC filtration was a viable technology for direct removal of HAAs from the pool water with a nominal efficiency of 57.7% by the filter while the chlorine residuals were 1.71 ± 0.90 mg/L during the study. THMs and TOC were not removed and thus were not considered as indicators of the effectiveness of BAC filtration. Increased EBCT in the range of 4.5 and 6.4 min led to improved HAA removal performance, which could be best fit by a logarithmic regression model. BAC filtration also affected the HAA speciation by removing more dichloroacetic acid (DCAA) than trichloroacetic acid (TCAA), resulting in a lower ratio of DCAA/TCAA in the filtered effluent. However, the observation of an overall constant ratio could be attributable to a complex formation and degradation mechanism occurring in swimming pools.

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1. Introduction

Haloacetic acids (HAAs) and trihalomethanes (THMs) as two major groups of disinfection by-products (DBPs) in chlorinated drinking water, have received significant concerns in decades due to their carcinogenic effects. They are formed upon the unintended reactions between the disinfectants and organic compounds in water, and the US Environmental Protection Agency (USEPA) has promulgated the Stage 1 and 2 Disinfectants/Disinfection Byproduct Rule (D/DBPR) to regulate the amount of total HAAs (THAAs) and total THMs (TTHMs) at maximum contaminant levels (MCLs) of 60 and 80 $\mu\text{g/L}$, respectively, in finished drinking water (USEPA, 1998, 2006). To prevent outbreak of waterborne disease, swimming pool water must also be disinfected at all times, and most countries do not have a specified regulatory limit for HAAs and THMs in swimming pools. In recent years, the database of identified DBPs in swimming pool water has expanded with a few toxic compounds at trace levels (Zwiener et al., 2007; Yang and Zhang, 2013; Wang et al., 2013; Liu and Zhang, 2014). Despite that the best known and most intensively investigated THMs remained at relatively low concentrations (18–133 $\mu\text{g/L}$) in swimming pool water (Fantuzzi et al., 2001; Chu and Nieuwenhuijsen, 2002), surveys around the world have reported that the THAA concentrations in swimming pools could be higher than 6800 $\mu\text{g/L}$, which is several orders of magnitude higher than the above-mentioned MCL (Tang, 2011; Simard et al., 2013; Wang et al., 2014; Chowdhury et al., 2014; Teo et al., 2015). As these DBPs can be taken up through dermal absorption (Xiao et al., 2012), ingestion, and inhalation (Lee et al., 2009), increasing attention is being focused on the potential health risks associated with exposure to such high levels of DBPs for pool users and attendants at indoor and outdoor pools (Kogevinas et al., 2010; Liviac et al., 2010; Richardson et al., 2010). It is therefore highly desirable to develop technologies on effective control of HAAs in swimming pool water. Nevertheless, this information is limitedly presented in current literature and should be extensively studied.

Existing control measures for DBPs in swimming pools consist of strategies on indirect removal focusing on DBP precursors and direct removal targeting on DBPs. The DBP precursors in swimming pools have been associated with the natural organic matter (NOM) in water and the bather-introduced substances such as hair, sweat, urine, saliva, skin, and cosmetics (Kim et al., 2002; Zwiener et al., 2007; Tang, 2011). It is easier to control the DBPs by limiting these precursors from entering the pools, and the beneficial strategies include reducing the anthropogenic inputs by enforcing showering prior to the pool use and using groundwater as the source water for lower levels of NOM. In addition, some precursors can be removed with particles during conventional sand filtration (Hansen et al., 2012) or ultrafiltration with membranes (Glauner et al., 2005; Barbot and Moulin, 2008). However, it is also noted that other precursors in the dissolved form largely remain in the water and continuously react with the disinfectant, causing a great potential in DBP formation (Liu et al., 2014). Thus, the direct removal of the formed DBPs, which can be pursued via physical, chemical and biological processes, is essential. Among available physical processes on direct removal of DBPs, diffused aeration has been used for THM control (Brooke and Collins, 2011). However, it is poorly documented on the removal of the less-volatile HAAs (Tang, 2011). Besides chemical processes such as Fe(0) reduction (Hozalski et al., 2001; Zhang et al., 2004; Tang et al., 2013) and UV irradiation (Weng et al., 2012), a typical biological process involves the use of a biologically active carbon (BAC) filter (Zhou and Xie, 2002; Xie and Zhou, 2002; Uhl and Hartmann, 2005; Tung et al., 2006; Tang et al., 2013) and the advantage of a BAC system is the ability of removing both precursors and HAAs which are firstly adsorbed into the macropores, where they are detained for the biological degradation by the attached bacteria (Kalkan et al., 2011). These findings, however, were largely based on bench-scale experiments from the treatment of dechlorinated water, and it is unclear whether the BAC filtration is applicable to the treatment of the chlorinated swimming pool water.

In this work, a BAC filter was set up on site for the treatment of chlorinated water in a swimming pool. The objectives of this research were to explore the direct removal technology in the control of HAAs in the chlorinated pool water and to investigate the impact of a short empty bed contact time (EBCT) on the BAC filtration performance. The results of this study will add to the existing knowledge an implementation case of BAC filtration of swimming pool water for HAA control.

2. Materials and methods

2.1. The swimming pool

The swimming pool under investigation was an outdoor pool with an effective volume of approximately 68 m^3 . Ground water was used as source water and it was disinfected periodically with a handful of commercially available chlorine tablets (calcium chlorite), which are able to produce 90% available stabilized chlorine prior to any swimming activities. The free, combined and total chlorine residuals, pH and water temperature during the investigation period were summarized in Table 1.

2.2. The BAC filter

Fig. 1 shows the schematic diagram of the BAC filter setup at the pool and there is no other filter in the loop. A 2-meter high filter was assembled with PVC columns with a diameter of 10.16 cm (a cross-sectional area of 81.0 cm^2) and BAC medium was loaded to a depth of 0.9 m. One bed volume (BV) of the BAC filter was $7.3 \times 10^{-3} \text{m}^3$. The swimming pool water was pumped to the BAC filter, and a gravity filtration with overflow was maintained to result in a constant water head of 0.9 m above the filter medium at all examined EBCTs. The BAC medium, which had been on line for 5 years treating ozonated water, was obtained from a full-scale water treatment plant (Hershey, Pennsylvania, USA). Since the medium was already biologically active, an acclimation period was not required. The valve installed in the filter outlet pipe was used to adjust the flow rate to maintain an EBCT of 5.8 min. While the treatment was in progress, other four EBCTs (4.5, 4.7, 5.1 and 6.4 min) were also investigated to explore their impact on the BAC filtration performance. To prevent short-circuiting of the intake flow and filter effluent, the filter influent was obtained from the farther end of pool.

2.3. Sample collection

Besides the on-site measurements of temperature, flow rate and chlorine residuals, the filter influent (i.e. pool water samples) and filter effluent samples were collected for the analyses of DBPs. Pre-cleaned vials (40 mL) loaded with ammonia chloride were used for the collection of swimming pool water samples with no head space. The ammonia chloride quenched the chlorine residual by converting chlorine to chloramines to stop further reactions between the chlorine and organic matter. The vials were placed in an icebox and transported to the laboratory for storage at 4 $^{\circ}\text{C}$ in a refrigerator. The samples were extracted and analyzed within 14 days.

2.4. Analytical methods

Free and total chlorine residuals were measured with the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method using a portable colorimeter (Model DR890, HACH, Colorado, USA). TOC was measured with a TOC analyzer (O.I. Analytical, Model 1010, Texas, USA). The HAA extraction and analysis followed the protocol of EPA method 552.3. In short, concentrated sulfuric acid (1.5 mL) was added to 30 g of sample followed by addition of 3 mL methyl tertiary butyl ether (MTBE) spiked with 1,2-dibromopropane as the internal standard.

Table 1
Water quality parameters of the swimming pool water before and after filtering 5400 bed volumes of the pool water by BAC.

Water quality parameter	Pool water before BAC filtration		Pool water after BAC filtration	
	Arithmetic mean	Standard deviation	Arithmetic mean	Standard deviation
Water temperature [°C]	23.8	2.1	25.7	0.6
pH	7.3	0.1	7.2	0.1
Free chlorine [mg/L]	1.41	0.55	1.59	0.76
Combined chlorine [mg/L]	0.14	0.19	0.19	0.1
Total chlorine [mg/L]	1.55	0.68	1.78	0.79
TOC [mg/L]	1.04	0.12	1.09	0.18
Total THMs [µg/L]	56	6	51	16
Total HAAs [µg/L]	1364	37	1026	26

Sodium sulfate (approximately 12 g) was then added to facilitate the extraction. The MTBE extract (1 mL) was mixed with 10% sulfuric acid–methanol mix (1 mL) and incubated for 2 h at 50 °C for HAA derivatization. After derivatization, the solution was back-extracted with 4 mL of 10% sodium sulfate solution to remove excess methanol. For THM analysis, EPA method 551.1 was followed and the extraction followed the above-mentioned protocols using pentane without the pre-extraction acidification and post-extraction methylation processes. The extracted HAA samples were analyzed by gas chromatograph (GC, Hewlett Packard 6890) equipped with a DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). GC with a DB-1 capillary column (30 m × 0.32 mm i.d., 1.0 µm film thickness) was used for the analysis of THMs. The temperature ramping programs had been described elsewhere (Tang et al., 2012). The reported values of THAAs were the sum of monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA) and dibromoacetic acid (DBAA) while those of TTHMs were the sum of chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (BF). The minimum reporting level (MRL) of each species was 1 µg/L.

3. Results and discussion

3.1. HAA profile in the pool

Fig. 2 shows the THAA profile in the pool water as the BAC filtration progressed. The THAA concentration in the pool at the start of the experiment was 1396 µg/L. As the BAC filter treated more BVs of the pool water, the THAA concentration decreased consistently and a linear correlation was obtained between the percent of treated volumes and the percent of THAA removal from the pool water, with an R^2 of

0.8194 (Fig. 2). After filtering 58% of the pool water (5400 BV), the THAA concentration was decreased to 1033 µg/L (26.0% removal from the pool water). The results indicated that the BAC filtration was able to remove HAAs from the chlorinated pool water. Assuming that there was 100% removal of THAAs by the BAC filter, the percent of THAA removal from the pool water would be equal to the percent of treated volumes. This could be described by the diagonal line ($y = x$) that hypothetically denotes complete removal of THAAs by BAC filtration. The actual regression line ($y = 0.5765x$) indicated a nominal THAA removal of 57.7% by BAC filtration during the entire investigation period.

The THMs, however, did not show any removal from the pool water, and their concentrations before and after the BAC filtration were 56 ± 6 µg/L and 51 ± 16 µg/L, respectively (Table 1). The non-removal of THMs could be associated with low biodegradation of THMs due to their biologically stable characteristics compared to HAAs. The low concentrations of THMs were also attributable to the open system of the swimming pool, which led to fast volatilization upon formation. TOC was not reduced from the pool water either. The concentrations before and after the BAC filtration were 1.04 ± 0.12 mg/L and 1.09 ± 0.18 mg/L, respectively. It can be deduced that THMs and TOC were not indicators of the effectiveness of the BAC filtration for swimming pool water treatment. Simard et al. (2013) reported a poor correlation between TOC and the occurrence of HAAs in outdoor pool water. Similar observations existed between TOC and THMs (Lou et al., 2010). The non-removal of TOC from the pool could be attributed to the introduction of anthropogenic pollutants by bathers (Kim et al., 2002) and the detachment of biofilm from the BAC medium (Butterfield et al., 2002).

It was noted that the removal of the HAAs from the pool water was obtained in presence of chlorine residuals in the pool water, and the concentrations of free, combined and total chlorine residuals during the BAC filtration were maintained at 1.55 ± 0.84 , 0.16 ± 0.16 , and 1.71 ± 0.90 mg/L, respectively, by pool attendants. This study

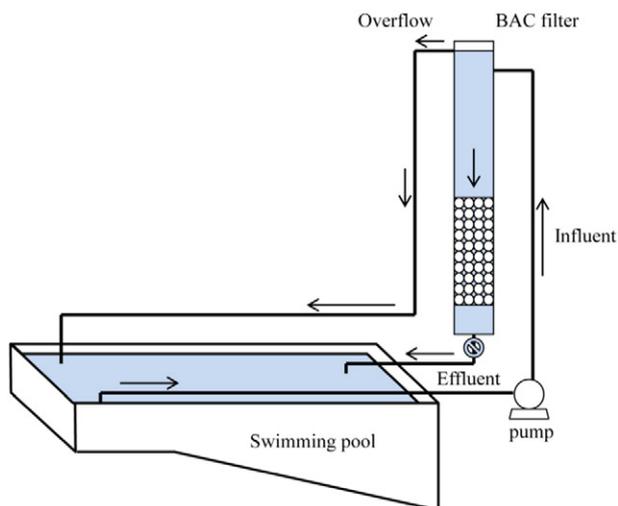


Fig. 1. Schematic diagram of the BAC filter setup at the pool (sizes are not to scale).

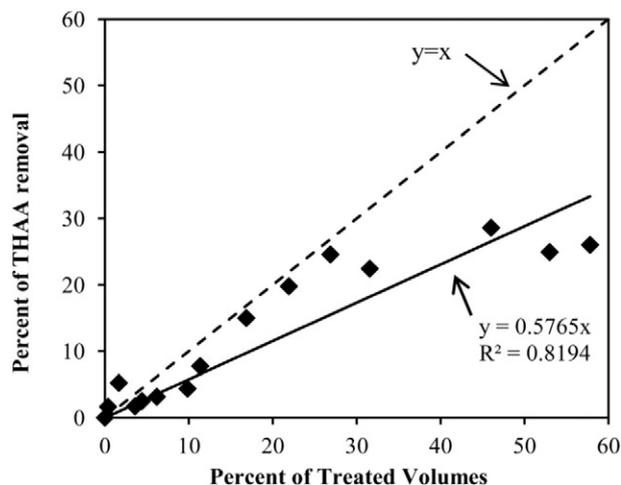


Fig. 2. Percent of THAA removal from the pool as a function of percent of treated volumes of the pool.

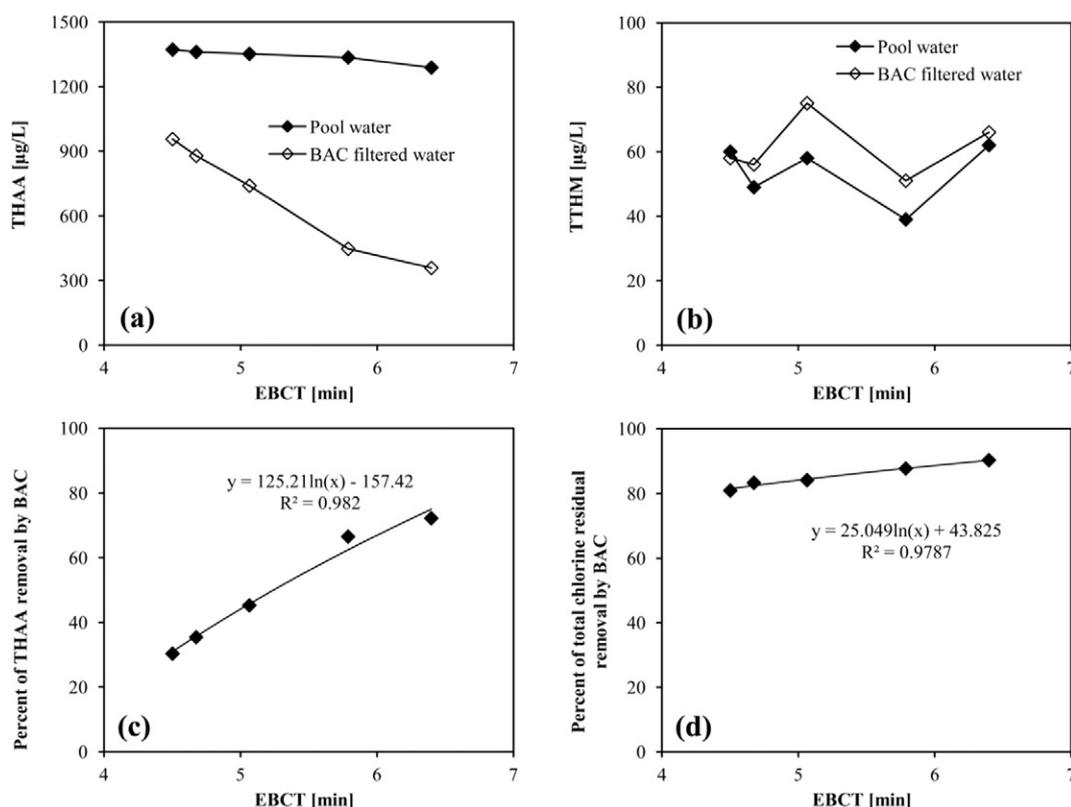


Fig. 3. Effect of EBCT on BAC filtration performance: (a) THAA; (b) TTHM; (c) percent of THAA removal by BAC; and (d) percent of total chlorine residual removal by BAC.

demonstrated the ability of BAC filtration on removing HAAs from the chlorinated pool water under the influence of the above-mentioned concentrations of chlorine residuals.

3.2. Performance of the BAC filtration

Fig. 3 shows the performance of the BAC filtration for removals of THAAs, TTHMs and total chlorine residuals as measured in the effluent samples collected from the filter outlet. The patterns of THAAs and total chlorine residuals (Fig. 3a, c and d) as a function of EBCT revealed the BAC filtration was able to remove a portion of HAAs in the presence of chlorine residuals in the examined range of EBCT from 4.5 to 6.4 min. A longer EBCT resulted in greater removals of THAAs and total chlorine residuals in the filter effluent. Ratasuk et al. (2008) reported similar findings in absence of the disinfectant – ozone and suggested an EBCT of at least 20 min to remove 90–100% of HAAs. Wu and Xie (2005) showed an EBCT of 5 min could be used for dechlorinated water above 10 °C. The major difference of the experimental conditions between our study and the two literatures was the presence of the disinfectant – chlorine. Because the chlorine residuals in the pool water have to be maintained at certain levels (e.g. 0.3–0.6 mg/L in Germany's regulations) for hygienic considerations in most swimming pools, it is important to operate the BAC filter under the influence of the disinfectant at these levels. Despite that the BAC filtration may not remove all chlorine residuals in the examined range of EBCT (Fig. 3d), decent removals of HAAs were still observed. As the EBCT increased from 4.5 to 6.4 min, the percent of THAA removal by the BAC increased from 30.3% to 72.2%, and the correlation could be best fit by a logarithmic regression model with an R^2 of 0.982 (Fig. 3c). For the percent removal of total chlorine residual, a logarithmic regression with an R^2 of 0.9787 was observed (Fig. 3d). Buchanan et al. (2008) also studied a BAC system and reported effective removal of another residual disinfectant – hydrogen peroxide produced by VUV irradiation. It is speculated that as residual disinfectants were removed by a greater extent at a longer EBCT, their

negative impact on the established biofilm in the BAC could be minimal. Uhl and Hartmann (2005) found that the combined chlorine penetrates deeper in the BAC filter bed than the free chlorine does. The removal of HAAs may also benefit from the low concentrations of combined chlorine (0.16 ± 0.16 mg/L) in the pool water. In addition, there were beneficial aspects of the disinfectants' presence, which were the breakup of the recalcitrant organics and production of more assimilable organic carbon (AOC) for the bacteria growth in the BAC medium (Butterfield et al., 2002; Lou et al., 2009).

The pathway of THMs in BAC filtration was more obscure compared to that of HAAs. In contrast to Lou et al. (2014) who reported removals of both THMs and HAAs from treated drinking water by a BAC filter, no trend of THM removal from the pool water was observed by the BAC filter in our study (Fig. 3b). Different from HAAs with a confirmed pathway of biodegradation (Tung et al., 2009), THMs could be affected by a possible carbon adsorption mechanism. Since the BAC medium used in this research had been on line in a full-scale water treatment plant for 5 years and the surface area of the activated carbon may have been exhausted, a removal mechanism of direct carbon adsorption was considered less likely (Tung et al., 2006). In addition, the TTHM concentrations in filter effluent were sometimes observed to be even higher than those in the filter influent. This might be attributed to the leaching of soluble microbial products (Liu et al., 2014), which reacted with residual chlorine in the pool water to form additional THMs.

3.3. Effect of BAC filtration on HAA speciation

Fig. 4 shows the removal of each HAA species by the BAC filtration. DCAA, TCAA, BCAA and DBAA were observed in the pool water and most filter effluent samples. DCAA and TCAA were the predominant HAA species and their concentrations in the pool water were at levels of 500 and 800 µg/L, respectively. As the EBCT increased from 4.5 to 6.4 min, the concentrations of DCAA in the filter effluent decreased from 299 to 88 µg/L (Fig. 4a) while those of TCAA decreased from 644

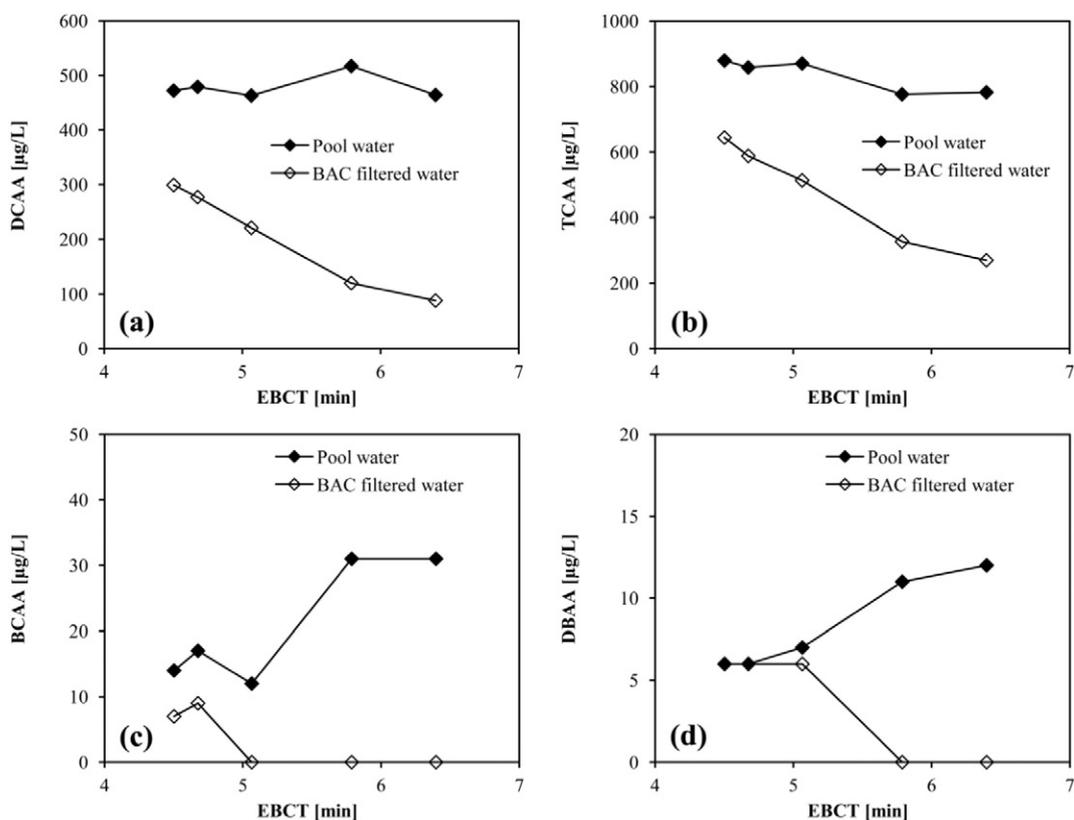


Fig. 4. Effect of BAC filtration on HAA speciation: (a) DCAA; (b) TCAA; (c) BCAA; and (d) DBAA.

to 270 µg/L (Fig. 4b). The ratios of DCAA/TCAA were compared between the pool water and the BAC filtered water, and it was found that the BAC filtration could reduce the ratios from 0.54 to 0.46 at an EBCT of 4.5 min and from 0.59 to 0.33 at an EBCT of 6.4 min (Fig. 5). The lowered ratios of DCAA/TCAA implied the preferential removal of DCAA by the BAC filtration. This observation agreed with Zhou and Xie (2002) who attributed this phenomenon to the slower degradation of TCAA by BAC filtration. It was also found that an increased EBCT would enlarge the difference between the DCAA and TCAA and result in a much smaller ratio. Fig. 4c and d show that BCAA and DBAA as brominated species of HAAs can be completely removed by the BAC filtration at a longer EBCT. Complete removal of BCAA was observed at an EBCT of higher than 5.1 min while that of DBAA was observed at an EBCT of higher than 5.8 min.

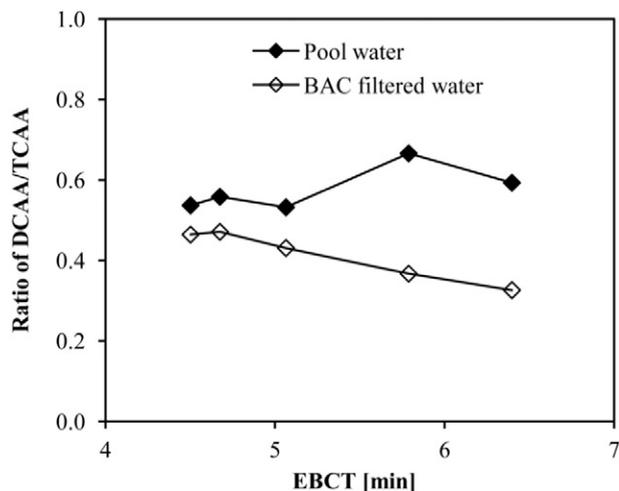


Fig. 5. Effect of BAC filtration on the ratio of DCAA/TCAA.

It is noted that although the BAC filtration preferentially removed DCAA over TCAA as measured in filter effluent samples, the ratio of DCAA/TCAA in the pool did not demonstrate much difference while treating 5400 BV of the pool water as revealed in Fig. 6. The overall constant ratio of DCAA/TCAA could be due to a complex formation and degradation mechanism occurring in the pool. Tang (2011) reported a higher formation potential of DCAA than TCAA for certain anthropogenic pollutants upon chlorination, which may offset the amount of the preferential DCAA removal by the BAC filter. The outdoor pool was also under the influence a series of physicochemical processes such as temperature change, prolonged exposure to UV, and enhanced volatility to water agitation by bathers which may all affect the DBP speciation (Liu and Reckhow, 2015; Lifongo et al., 2004; Tang, 2011).

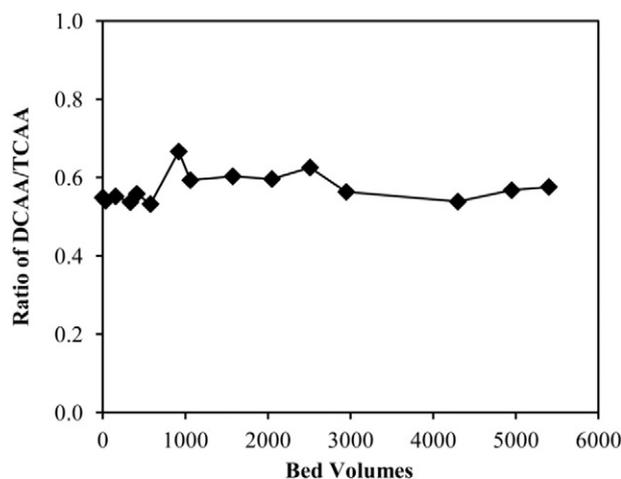


Fig. 6. The ratio of DCAA/TCAA in the pool during the BAC filtration.

3.4. Implications

The results of the study are significant to the water industry – BAC filters can be used for the direct control HAAs in the chlorinated swimming pool water. We have tested pool water with total chlorine residuals of 1.71 ± 0.90 mg/L and found effective removals of HAAs. Moreover, in contrast to a long EBCT which limits the practical application of BAC filtration for the treatment of a large volume of swimming pool water, the research demonstrated the HAA removal ability at short EBCTs as low as 4.5 min; while at an average EBCT of 5.8 min for the actual operation on site, the predicted THAA removal by the BAC filter with the logarithmic regression was 62.7% (Fig. 3c). Noticeably, this number was higher than the nominal removal of 57.7% as observed from the pool water (Fig. 2), implying production of new HAAs in the pool while the treatment was in progress. Aggazzotti et al. (1995) suggested the number of pool users had a correlation with the levels of chloroform in swimming pools. The continuous use of the pool by swimmers during the study might partially explain the small discrepancy between the two numbers while other uncertainty came from the complex formation and degradation mechanism of DBPs in swimming pools which is summarized as follows: (1) The consistent presence of chlorine residuals in pools maximize the formation of DBPs from their anthropogenic precursors (Kim et al., 2002); (2) the detachment of biofilm from the BAC filter and the formation of soluble microbial products adds to the DBP levels upon chlorination (Liu et al., 2014); (3) water temperature and pH affect the DBP formation, and a high water temperature and an alkaline pH favor the formation of DCAA upon chlorination (Liu and Reckhow, 2015; Hua and Reckhow, 2012); (4) DBPs in swimming pool water can escape to the atmosphere and the volatilization rates determined from the respective Henry's law constant of each species are different (Brooke and Collins, 2011); (5) DBPs – especially TCAA, can be degraded by UV radiation (Lifongo et al., 2004); and (6) DBPs – especially HAAs, can be degraded by bacteria with a BAC filter. Despite that a steady decrease of HAA concentration was observed in the pool water with chlorine residuals of 1.71 ± 0.90 mg/L during the BAC filtration under the influence of the above-mentioned mechanisms, this research, however, did not explore the performance of BAC filtration for some U.S. swimming pools with observed chlorine residuals above 3 mg/L (Kanan and Karanfil, 2011). Further research is needed to examine those pools with the BAC filtration.

4. Conclusions

BAC filtration is a viable strategy for direct removal of HAAs from chlorinated swimming pool water. A steady decrease of HAA concentration was achieved during on-site filter operation at short EBCTs as low as 4.5 min while chlorine residuals were present in the pool water. THMs and TOC were not removed and thus were not considered as indicators of the effectiveness of BAC filtration. Increased EBCT in the range of 4.5 and 6.4 min led to improved HAA removal performance, which could be best fit by a logarithmic regression model. BAC filtration also affected the HAA speciation by removing more DCAA than TCAA, resulting in a lower ratio of DCAA/TCAA in the filtered effluent. However, the observation of an overall constant ratio was attributable to a complex formation and degradation mechanism occurring in swimming pools.

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References

- Aggazzotti, G., Fantuzzi, G., Righi, E., Predieri, G., 1995. Environmental and biological monitoring of chloroform in indoor swimming pools. *J. Chromatogr. A* 710, 181–190.
- Barbot, E., Moulin, P., 2008. Swimming pool water treatment by ultrafiltration–adsorption process. *J. Membr. Sci.* 314, 50–57.
- Brooke, E., Collins, M.B., 2011. Posttreatment aeration to reduce THMs. *J. Am. Water Works Assoc.* 103, 84–96.
- Buchanan, W., Roddick, F., Porter, N., 2008. Removal of VUV pre-treated natural organic matter by biologically activated carbon columns. *Water Res.* 42, 3335–3342.
- Butterfield, P.W., Camper, A.K., Ellis, B.D., Jones, W.L., 2002. Chlorination of model drinking water biofilm: implications for growth and organic carbon removal. *Water Res.* 36, 4391–4405.
- Chowdhury, S., Alhooshani, K., Karanfil, T., 2014. Disinfection byproducts in swimming pool: occurrences, implications and future needs. *Water Res.* 53, 68–109.
- Chu, H., Nieuwenhuijsen, M.J., 2002. Distribution and determinants of trihalomethane concentrations in indoor swimming pools. *Occup. Environ. Med.* 59, 243–247.
- 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.
- Glauner, T., Waldmann, P., Frimmel, F.H., Zwiener, C., 2005. Chlorination of model drinking water – fractionation and genotoxicological characterization of organic constituents. *Water Res.* 39, 4494–4502.
- Hansen, K.M.S., Willach, S., Mosboek, H., Andersen, H.R., 2012. Particles in swimming pool filters – does pH determine the DBP formation? *Chemosphere* 87, 241–247.
- Hozalski, R.M., Zhang, L., Arnold, W.A., 2001. Reduction of haloacetic acids by Fe(0): implications for treatment and fate. *Environ. Sci. Technol.* 35, 2258–2263.
- Hua, G., Reckhow, D.A., 2012. Effect of alkaline pH on the stability of halogenated DBPs. *J. Am. Water Works Assoc.* 104, E107–E120.
- Kalkan, C., Yapsakli, K., Mertoglu, B., Tufan, D., Saatci, A., 2011. Evaluation of biological activated carbon (BAC) process in wastewater treatment secondary effluent for reclamation purposes. *Desalination* 265, 266–273.
- 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.
- Kim, H., Shim, J., Lee, S., 2002. Formation of disinfection by-products in chlorinated swimming pool water. *Chemosphere* 46, 123–130.
- Kogevinas, M., Villanueva, C.M., Font-Ribera, L., Liviak, D., Bustamante, M., Espinoza, F., Nieuwenhuijsen, M.J., Espinosa, A., Fernandez, P., DeMarini, D.M., 2010. Genotoxic effects in swimmers exposed to disinfection by-products in indoor swimming pools. *Environ. Health Perspect.* 118, 1531–1537.
- Lee, J., Ha, K., Zoh, K., 2009. Characteristics of trihalomethane (THM) production and associated health risk assessment in swimming pool waters treated with different disinfection methods. *Sci. Total Environ.* 407, 1990–1997.
- Lifongo, L.L., Bowden, D.J., Brimblecombe, P., 2004. Photodegradation of haloacetic acids in water. *Chemosphere* 55, 467–476.
- Liu, B., Reckhow, D.A., 2015. Disparity in disinfection byproducts concentration between hot and cold tap water. *Water Res.* 70, 196–204.
- Liu, J., Zhang, X., 2014. Comparative toxicity of new halophenolic DBPs in chlorinated saline wastewater effluents against a marine alga: halophenolic DBPs are generally more toxic than haloaliphatic ones. *Water Res.* 65, 64–72.
- Liu, J., Li, X., Xie, Y.F., Tang, H., 2014. Characterization of soluble microbial products as precursors of disinfection byproducts in drinking water supply. *Sci. Total Environ.* 472, 818–824.
- Liviak, D., Wagner, E.D., Mitch, W.A., Altonji, M.J., Plewa, M.J., 2010. Genotoxicity of water concentrates from recreational pools after various disinfection methods. *Environ. Sci. Technol.* 44, 3527–3532.
- Lou, J., Chang, T., Huang, C., 2009. Effective removal of disinfection by-products and assimilable organic carbon: an advanced water treatment system. *J. Hazard. Mater.* 172, 1365–1371.
- Lou, J., Huang, C., Han, J., Huang, Y., 2010. Generation of disinfection by-products (DBPs) at two advanced water treatment plants. *Environ. Monit. Assess.* 162, 365–375.
- Lou, J., Chang, C., Chen, W., Tseng, W., Han, J., 2014. Removal of trihalomethanes and haloacetic acids from treated drinking water by biological activated carbon filter. *Water Air Soil Pollut.* 225, 1851.
- Ratasuk, C., Kositanont, C., Ratanatamskul, C., 2008. Removal of haloacetic acids by ozone and biologically active carbon. *ScienceAsia* 34, 293–298.
- Richardson, S.D., DeMarini, D.M., Kogevinas, M., Fernandez, P., Marco, E., Lourencetti, C., Ballesté, C., Heederik, D., Meliefste, K., McKague, A.B., 2010. What's in the pool? A comprehensive identification of disinfection by-products and assessment of mutagenicity of chlorinated and brominated swimming pool water. *Environ. Health Perspect.* 118, 1523–1530.
- Simard, S., Tardif, R., Rodriguez, M.J., 2013. Variability of chlorination by-product occurrence in water of indoor and outdoor swimming pools. *Water Res.* 47, 1763–1772.
- Tang, H., 2011. Disinfection Byproduct Precursors From Wastewater Organics: Formation Potential and Influence of Biological Treatment Processes. The Pennsylvania State University, University Park, Pennsylvania (dissertation for the doctoral degree).
- Tang, H.L., Regan, J.M., Chen, Y., Xie, Y.F., 2012. Disinfection by-product formation potentials in wastewater effluents and their reductions in a wastewater treatment plant. *J. Environ. Monit.* 14, 1515–1522.
- Tang, S., Wang, X., Yang, H., Xie, Y.F., 2013. Haloacetic acid removal by sequential zero-valent iron reduction and biologically active carbon degradation. *Chemosphere* 90, 1563–1567.
- Teo, T.L.L., Coleman, H.M., Khan, S.J., 2015. Chemical contaminants in swimming pools: occurrence, implications and control. *Environ. Int.* 76, 16–31.
- Tung, H.H., Unz, R.F., Xie, Y.F., 2006. HAA removal by GAC adsorption. *J. Am. Water Works Assoc.* 98, 107–112.

- Tung, H.H., Unz, R.F., Xie, Y.F., 2009. Evidences of HAAs biodegradation in GAC filtration. *J. Environ. Manag.* 19, 59–66.
- Uhl, W., Hartmann, C., 2005. Disinfection by-products and microbial contamination in the treatment of pool water with granular activated carbon. *Water Sci. Technol.* 52, 71–76.
- USEPA (US Environmental Protection Agency). Stage 1 disinfectants and disinfection byproducts rule. Quick reference guide. EPA 816-F-02-021, Washington; 1998.
- USEPA. Stage 2 disinfectants and disinfection byproduct rule. 40 CFR Parts 9,141, and 142, EPA-HQ-OW-2002-0043; FRL-8012-1, RIN 2040-AD38, Washington; 2006.
- Wang, W., Qian, Y., Boyd, J.M., Wu, M., Hrudey, S.E., Li, X.F., 2013. Halobenzoquinones in swimming pool waters and their formation from personal care products. *Environ. Sci. Technol.* 47, 3275–3282.
- Wang, X., Leal, G., Zhang, X., Yang, H., Xie, Y., 2014. Haloacetic acids in swimming pool and spa water in the United States and China. *Front. Environ. Sci. Eng.* 8, 820–824.
- Weng, S., Li, J., Blatchley III, E.R., 2012. Effects of UV₂₅₄ irradiation on residual chlorine and DBPs in chlorination of model organic-N precursors in swimming pools. *Water Res.* 46, 2674–2682.
- Wu, H., Xie, Y.F., 2005. Effects of EBCT and water temperature on HAA removal using BAC. *J. Am. Water Works Assoc.* 97, 94–101.
- Xiao, F., Zhang, X., Zhai, H., Lo, I.M.C., Tipoe, G.L., Yang, M., Pan, Y., Chen, G., 2012. New halogenated disinfection byproducts in swimming pool water and their permeability across skin. *Environ. Sci. Technol.* 46, 7112–7119.
- Xie, Y.F., Zhou, H., 2002. Use of BAC for HAA removal: part 2, column study. *J. Am. Water Works Assoc.* 94, 126–134.
- Yang, M., Zhang, X., 2013. Comparative developmental toxicity of new aromatic halogenated DBPs in a chlorinated saline sewage effluent to the marine polychaete *Platynereis dumerilii*. *Environ. Sci. Technol.* 47, 10,868–10,876.
- Zhang, L., Arnold, W.A., Hozalski, R.M., 2004. Kinetics of haloacetic acid reactions with Fe(0). *Environ. Sci. Technol.* 38, 6881–6889.
- Zhou, H., Xie, Y.F., 2002. Using BAC for HAA removal: part 1, batch study. *J. Am. Water Works Assoc.* 94, 194–200.
- Zwiener, C., Richardson, S.D., De Marini, D.M., Grummt, T., Glauner, T., Frimmel, F.H., 2007. Drowning in disinfection byproducts? Assessing swimming pool water. *Environ. Sci. Technol.* 41, 363–372.