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High potential for the formation of haloacetic acids in the Karoon River water in Iran

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Abstract The impact of the total organic carbon (TOC), chlorine dosage, water temperature, reaction time, pH, and seasonal variation on the formation of haloacetic acids (HAAs) in the Karoon River in Iran was studied. The results showed that dichloroacetic acid and trichloroacetic acid were the most detected HAA₅. The HAA₅ formation potential (HAA₅FP) levels in the Karoon River water in spring time, when the water TOC content exceeded 4 mg/L, were 1.38 times higher than during the winter season, when the water TOC content was below 3.5 mg/L. There was not a strong correlation between the HAA₅FP and the residence time for the Karoon River water. For the range

of the water temperatures studied, there was little variation in the HAA₅FP in cold water, but in warmer water, the values of the HAA₅FP varied quickly.

Keywords Haloacetic acid (HAA) · Karoon River · Seasonal variation · Chlorine · pH

Introduction

HAAs, one of the most prevalent disinfection by-products (DBPs), include nine substances. Only five of these substances are currently regulated in the USA (USEPA 1998a). These five haloacetic acids (HAA₅) are monochloro- and monobromo-acetic acid, dichloro- and trichloroacetic acid, and dibromoacetic acid (MCAA, MBAA, DCAA, TCAA, and DBAA, respectively). The main species of HAA₅ in drinking water are DCAA and TCAA, and others are generally found at lower levels.

In most developed countries and in some developing countries such as Iran (ISIRI 1997), standards for the trihalomethane levels (0.56 mg/L) in drinking water have been established with drinking water regulations, but there is no limit in Iran for HAA₅. Recently, efforts were made to better document the occurrence of HAAs, which are the second most important group of chlorinated DBPs after THMs. This interest in conducting research on these compounds is associated with the fact that toxicological studies have established that exposure to HAAs favours the development of cancer in laboratory

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animals (Malliarou et al. 2005; Muellner et al. 2007). In addition, in a recent epidemiological study, King et al. (2005) reported an increased cancer risk in humans associated with high levels of HAAs in drinking water. Therefore, their presence in drinking water has given rise to health risk concerns. In the USA, the maximum contaminant level is 60 µg/L for the sum of the five HAA₅ (USEPA 1998b).

It was reported that the occurrence of DBPs in chlorinated water may vary significantly based on season and geographical location of water resources (Williams et al. 1997; Garcia-Villanova et al. 1997). These variations are due to changes in the raw and treated water quality as well as changes in the operational parameters related to the chlorination process (Abdullah et al. 2003). The operational parameters that influence the formation of HAAs in the treatment systems include chlorine dose and contact time, water temperature, pH, bromide levels, and TOC. It has been concluded that, in terms of water quality, the natural organic matter (NOM), especially the hydrophilic portion and amino acids, constitute important precursors for HAAs (Bond et al. 2009; Hwang et al. 2001).

HAAs are also ubiquitous environmental contaminants that are detected in snow, ice, fog, rain water, seawater, and freshwater (Manuel et al. 2004, 2007; Hanson and Solomon 2004). Water resources are the likely repository for these compounds in the environment due to their water solubility and low Henry's law constants Hanson and Solomon (2004). The climate changes considerably throughout the year in southern Iran, the watershed of the Karoon River. The winters are relatively short and cold, while the summers are long and generally very hot. Consequently, the differences in water temperature between winter and summer can be greater than 20 °C (see Table 1). As a result of the changes in the seasons occurring very rapidly,

there is a sudden watershed runoff associated with the snow melting in the spring and a relatively rapid decay of vegetation, which is a source of NOM in water, during the fall. These factors may contribute to the significant changes in the surface water quality, and depending on the operational adjustments during the treatment processes and chlorine disinfection, they may also contribute to the seasonal changes in the DBPs throughout the year. Because there is no limitation for HAAs in Iran, the collection of data related to HAAs in water utilities is not mandatory. Therefore, there is currently very little information concerning the factors affecting the formation of these compounds and the influence that seasonal conditions may have.

Because very little research has been performed to investigate HAA₅ concentrations in the drinking water resources, information about the concentrations of HAA₅ and their potential formation in Iranian waters is lacking. Therefore, the main purpose of this study was to assess the effects of some of the water quality and operational factors on the HAA₅FP in Iran's largest river, the Karoon River. The results of this paper will be useful in the future management of the water treatment plants that service millions of people living around this river. The results will also be important for future regulations in the Iran.

Materials and methods

Sampling strategy

The Karoon River is the longest river in Iran. It lies in western Iran and flows from the north to the south until it flows into the Persian Gulf. The Karoon River provides the drinking water source for many major cities and the Mahshahr petrochemical complex zone.

Table 1 The average values of the physical and chemical parameters of the Karoon River water at the Koot-e-Amir sampling point

Parameters	Summer	Fall	Winter	Spring
pH	7.3	7.45	7.14	7.22
TOC (mg/L)	4.01	4.77	3.42	4.35
Water temperature (°C)	28.05	12.47	8.22	13.39
Hardness (mg/L CaCO ₃)	149	163	124	131
Alkalinity (mg/L CaCO ₃)	133	137	103	107
Br ⁻ (µg/L)	135	181	123	131
Turbidity (NTU)	8.23	7.29	8.35	8.48

Samples were collected from the Karoon River water at the point of the Koot-e-Amir intake where the water is pumped to the water treatment plant in the Mahshahr petrochemical complex zone (Fig. 1). The general water characteristics of the Karoon River at the point of the Koot-e-Amir intake are presented in Table 1. To investigate the occurrence of the HAA₅FP within the raw water of the Karoon River, an intensive 12-week sampling program was undertaken during the fall season in 2009 and continued until the summer in 2010. The study period was 1 year from October 2009 to September

2010. Therefore, we collected 4 samples for each month and 12 samples for each season. For validation purposes, a total of 52 samples were collected from the raw water in the Karoon River at the point of the Koot-e-Amir intake. It was ensured that the sampling point was accessible for the entire year.

Experimental design

All experiments, including the determination the effects of factors such as seasonal variation, water temperature,

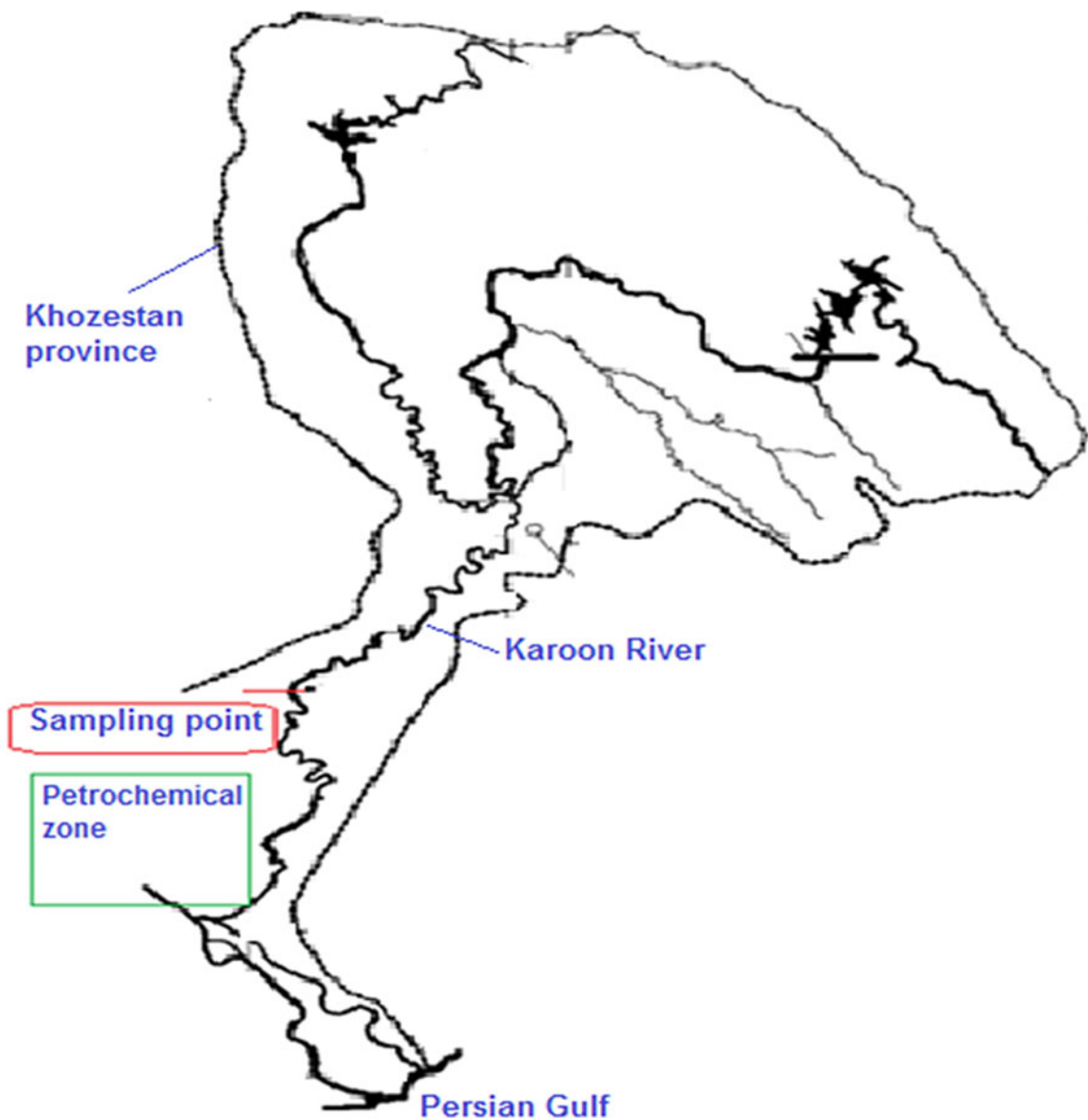


Fig. 1 The Karoon River and the sampling station at Koot-e-Amir

chlorine dosage, residence time, pH, and TOC on the HAA₅FP, were performed in batch mode. Specifically, 10 mg/L chlorine (see Fig. 4) was added to the raw water containing the original natural organic matter and then mixed at 125 rpm using a rotary shaker (Glas-col) under anaerobic conditions. The bottle was filled completely and capped without any headspace with a PTFE lined cap. A NOM stock solution was prepared by dissolving an aliquot of the Karoon River RO NOM isolate into double distilled water. The pH of the solution was not adjusted or controlled during the experiments. In another experiment, the water temperature was varied from 5 °C to 35 °C in a water bath. For the evaluation of pH effects, the initial pH of the water was adjusted to specific values by adding 1 N HCl/NaOH, and no acid or alkali was added for the control pH during following reaction. A stock of free chlorine (HOCl) solution was prepared from 5 % sodium hypochlorite (NaOCl) (Sigma-Aldrich), diluted to 1,000 mg/L as Cl₂ and stored in an aluminium foil-covered glass stoppered flask. It was periodically standardised by DPD titration. Then, the specified dosage of chlorine solution was added to the bottles. Aliquots (30 mL) of the samples were then collected from the bottles by pipette at various time intervals (5–120 h) for the analysis of the HAA₅. All of the experiments were conducted in triplicate, and the average values are presented.

Determination of the concentration HAA

The HAA₅ concentrations were determined using liquid–liquid extraction gas chromatography (GC) according to the EPA Method 552.2 (USEPA 1995). The sum of the five HAA (i.e., MCAA, BCAA, DBAA, DCAA, and TCAA) mass concentrations is reported as HAA₅ in micrograms per litre. Briefly, a 25-mL sample was adjusted to a pH value of 0.5 with sulphuric acid and then extracted with 4 mL of methyl *tert*-butyl ether (MTBE). Twelve grams of sodium sulphate was added to the samples to increase the extraction efficiency. The vial was sealed, shaken for 3 min, and allowed to stand for 5 min. The extracted compounds that were partitioned into the organic phase were then converted to their methyl esters by the addition of a methanol and sulphuric acid solution followed by heating for 2 h at 50 °C in a water bath. The solution was then cooled to 4 °C for 10 min, and the solvent phase was separated from the acidic methanol by adding 7 mL of a concentrated aqueous

solution of sodium sulphate. The aqueous phase was discarded. The extract was then neutralised with a saturated solution of sodium bicarbonate, and the 2-mL solvent layer was removed for analysis. The target analytes were identified and quantified by a temperature-programmable Hewlett-Packard 6890 GC using a capillary column with DB-1, 30 m × 0.32 mm I.D. × 1.0 μm film thicknesses and the μECD. The internal standard was 1,2,3-trichloropropane (Supelco), and the surrogate standard was 2,3-dibromopropionic acid (Supelco). At the beginning of each analytical run, solvent blanks and solvent samples containing the internal standard were injected to condition the GC and to verify that interferences were insignificant. Other quality assurance/quality control (QA/QC) procedures, such as QC check standards and matrix spikes, were performed throughout the analysis. Note that the detection limits for the analyses of the various HAA₅ species were 0.273, 0.242, 0.079, 0.204, and 0.066 μg/L for MCAA, DCAA, TCAA, MBAA, and DBAA, respectively.

Determination of the TOC

The TOC measurements were conducted with a Shimadzu TOC-5000 analyser equipped with a Pt catalyst on quartz wool (Shimadzu, Kyoto, Japan) and an auto-sampler according to the combustion infrared method as described in the Standard Methods of 3510 B (APHA and WEF 1998). At least three measurements were made for each sample to obtain multiple replicated for the results. Two calibration curves with potassium hydrogen phthalate at two different ranges were obtained by processing the peak areas.

Other analyses

The bromide ion concentration was determined using a Dionex ion chromatographic (IC) system (Sunnyvale, CA). The pH of the water samples was analysed with a pH meter. The chlorine residuals in the water samples were determined by the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method (APHA and WEF 1998). The turbidity was measured using a Hach 2100N Turbidimeter. The water temperature was determined directly with a water thermometer. The concentrations of hardness and alkalinity in solutions were measured by the titrimetric method as described

in sections of 2340 C and 2320 B of the Standard Methods, respectively (APHA and WEF 1998).

Results and discussion

Time dependency

The changes over time of the HAA₅FP and chlorine residuals with a TOC content of 5 mg/L and a chlorine dosage of 10 mg/L are depicted in Fig. 2. The value for the HAA₅ in a raw water sample from the Karoon River increased as the residence time was increased to 30 h, when the TOC content and the applied chlorine dose were in abundance (see Fig. 2). After that point, the HAA₅ sharply decreased. Generally, DBPs continue to form in drinking water as long as residual disinfectants and precursors are present (Singer and Reckhow 1999). However, the HAA₅ cannot consistently be related to water age because HAA₅ are known to biodegrade over time when the residual disinfectant is low.

This biodegradation might result in relatively low HAA₅ concentrations in the areas of the water distribution system where the disinfectant residuals are depleted (US EPA 2006). Baribeau et al. (2005) reported there was a greater concentration of HAA₅ in the treatment plant than in the distribution system. It is suggested that biodegradation is responsible for the decrease in HAA₅ with increased time. However, Fig. 2 also shows that the chlorine residual decreased with longer reaction times, especially at the 100 and 120 h time points, which are close to zero. Speight and Singer (2005) reported that an increase in the residence time leads to a decrease in the chlorine residual

in the water, which accounts for the low concentrations of HAA₅ observed. Unlike the formation of THMs, the mechanisms for the formation of HAAs are complex, and there are a number of rate-limiting steps (Ying-Xue et al. 2009). The concept of quick formers and slow formers that was previously mentioned in the literature for THMFP (Ying-Xue et al. 2009; Reckhow and Singer 1985) may not directly apply to the formation of HAAs in the chlorination of water sources. Finally, the concentration of HAA₅ decreased because HAA₅, which would decompose at a neutral pH value, formed (Zhang and Minear 2002). Furthermore, in presence of bromide in the water samples (see Table 1), the chlorination system became further complicated by HOBr, which once formed, reacts with ammonia and organic matter in a similar manner to chlorine, producing the corresponding bromamines and brominated organic compounds (Luong, Peters and Perry 1982). These are the causes for the weak or indefinite relationship between the formation of HAA₅ and the residence time for the Karoon River water.

The effects of water temperature

Temperature is an important factor involved in chemical reactions that may provide some insight into the mechanisms of the reactions evaluated in this study. Figure 3 illustrates that the rate of HAA₅ formation potential, which was measured in the reactions with 10 mg/L chlorine and the origin natural organic matters, increased linearly with increasing water temperature. After a reaction time of 60 h, the values of the HAA₅FP were 129.02 ± 12.12 and 326.11 ± 17.9 $\mu\text{g/L}$ for water temperatures at 5 °C and 35 °C,

Fig. 2 The variation of the HAA₅FP and the residual chlorine levels with reaction time in the Karoon River water (pH 7.33, chlorine dose 10 mg/L, TOC content 5 mg/L)

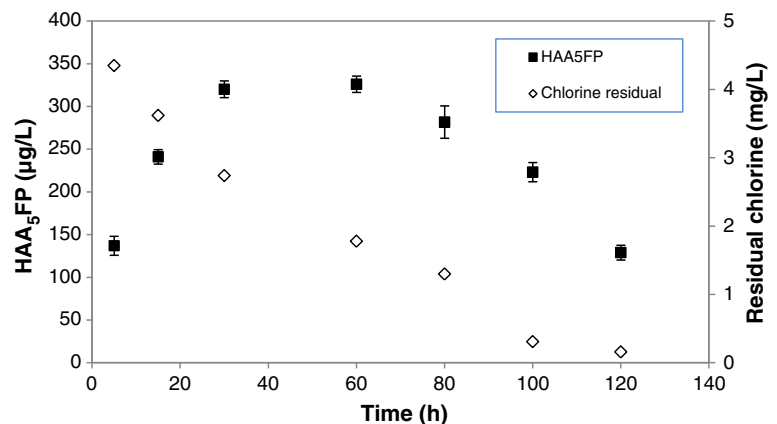
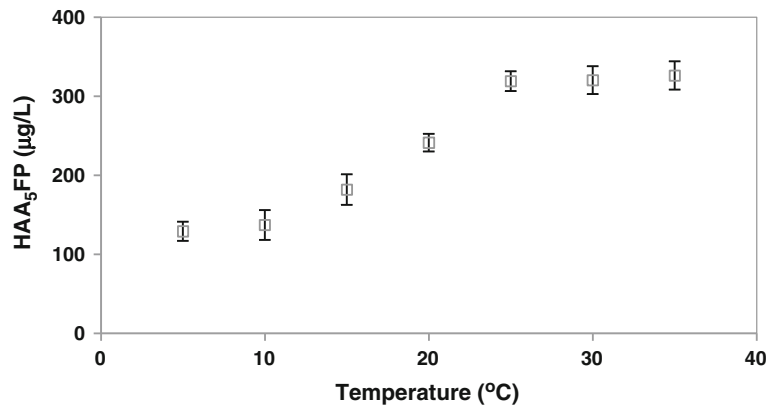


Fig. 3 The effect of water temperature on the HAA₅FP in the Karoon River (pH 7.4, chlorine dose 10 mg/L, TOC content 4.2 mg/L)



respectively. As shown in Fig. 3, a strong and definite correlation was obtained for the HAA₅FP and the water temperature. For the range of the studied water temperatures, the variation in the HAA₅FP was small in cold water (water temperature less than 15 °C), but the values of the HAA₅FP were drastically varied in warmer water (water temperature more than 15 °C). This result may be explained by an increase in the rate of the chlorine reaction with the TOC content.

It seems that temperature is not a critical factor affecting the HAA₅FP in the Karoon River water; otherwise, the amount of the HAA₅FP should be highest in the summer (see Fig. 6). Figure 3 clearly shows that the HAA₅FP increased with increasing temperature. If the products are relatively stable, their formation should increase rapidly with the increasing temperature. However, increasing the temperature also enhances the rates of the decomposition of the HAA₅ (Bixionget al. 2009; Xin et al. 2007). Therefore, the concentrations of these unstable DBPs depend on the relative rates of their

formation and decomposition. As illustrated in Fig. 3, the HAA₅ level was maintained when the temperature was increased above 25 °C. This trend could not be accounted for by HAA volatilisation, which would be the best reason for the acceleration in the HAA₅ decomposition rates compared to the formation rates at higher temperature because the HAA₅ are not volatile materials. Similar result were reported by Hrudey (2009) and Lu et al. (2009).

The effects of the chlorine dosage

Other experiments were conducted to determine the effects of the chlorination dosage on the HAA₅FP in the raw water from the Karoon River, and the results are shown in Fig. 4. As the chlorine content increases, the concentration of the HAA₅ increases. The concentration of the HAA₅ increased from 87.21 ± 10.1 µg/L with the 1 mg/L chlorine dose to more than 323.34 ± 8.54 µg/L with the 10 mg/L chlorine dose, while

Fig. 4 The effect of the initial chlorine dose on the HAA₅FP (pH 7.15, reaction time 60 h)

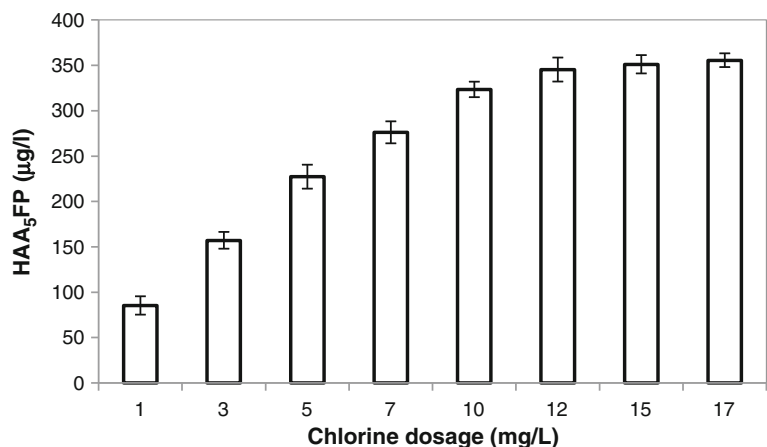
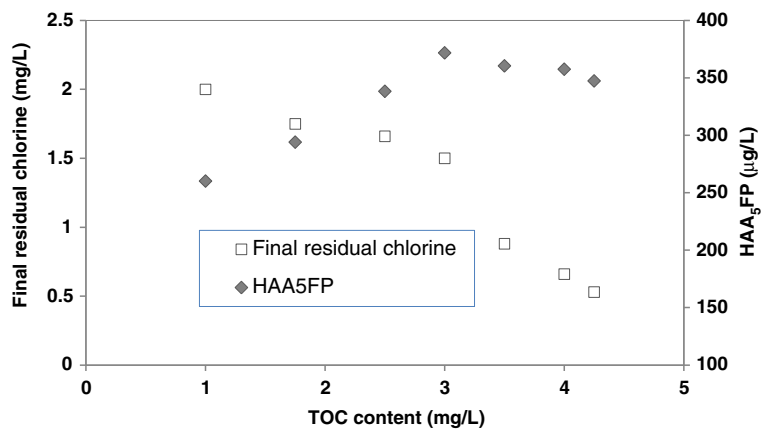


Fig. 5 The variation of the HAA₅FP and final residual chlorine level with the TOC content in the Karoon River water (pH 7.13, reaction time 60 h, chlorine dose 10 mg/L)



further increases in the chlorine doses to 12, 15, and 17 mg/L did not lead to a significant increase in the HAA₅FP (345.27±13.22, 351.09±10.09, and 355.65 ±7.56 µg/L, respectively). However, if the chlorine was unable to quench the further reaction of HAA₅ formation, the quantity of HAA₅ produced would change little. As reported by Jingyun (2010), the concentrations of the HAAs depend on their formation and decomposition rates. The greater chlorine doses did not change the HAA₅ concentration because the rates for the decomposition and the formation of the HAA₅ were equal or other DBPs were formed.

The effects of the TOC content

To study the effects of the total organic carbon on the formation of haloacetic acids in the Karoon River Water, the TOC was varied from 1 to 4.25 mg/L by diluting the

water samples with double distilled water free of TOC or by spiking the water samples with a NOM solution. The initial chlorine dose of the water samples was adjusted to 10 mg/L. Although the amount of the initial chlorine added was kept constant at 10 mg/L, the final residual chlorine was decreased from 2 to 0.53 mg/L as the TOC was increased.

The graphs for the HAA₅ formation potential and the final residual chlorine as a function of the TOC content in the Karoon River water are presented in Fig. 5. Overall, it was observed that the formation potential of the HAA₅ increases when the TOC was increased to 3, while further increases in the TOC did not lead to any significant changes in the HAA₅FP. The final residual chlorine values did decrease because the initial chlorine was consumed. The slightly negative slope in the formation potential curve of the HAA₅FP for the TOC greater than 3 may be due to a

Fig. 6 The seasonal variations of the HAA₅FP of the Karoon River water (reaction time 60 h, chlorine dose 10 mg/L)

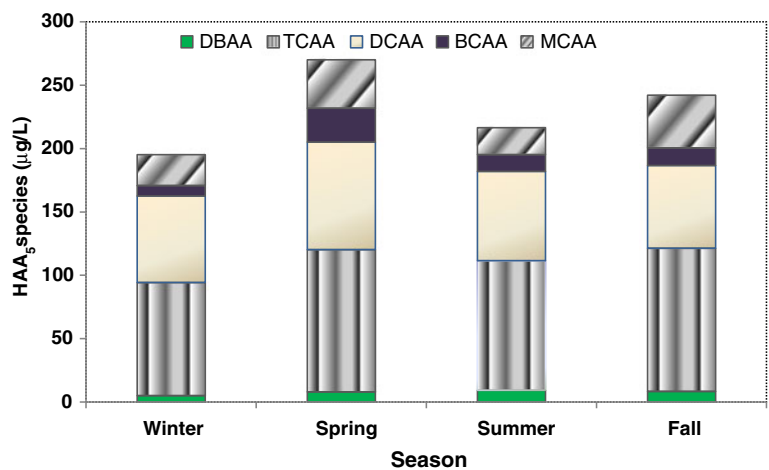
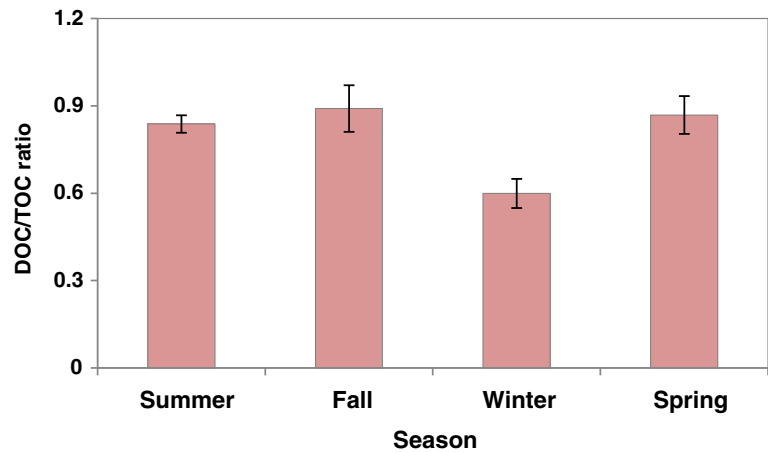


Fig. 7 The seasonal variations of the DOC concentration of the Karoon River water



decrease in the availability of residual chlorine, which might have been a result of its reaction with other constituents present in the water samples. Another probable reason is that the reaction between the TOC and the chlorine may have resulted in other DBPs such as THMs, as reported by Vedat et al. (2008).

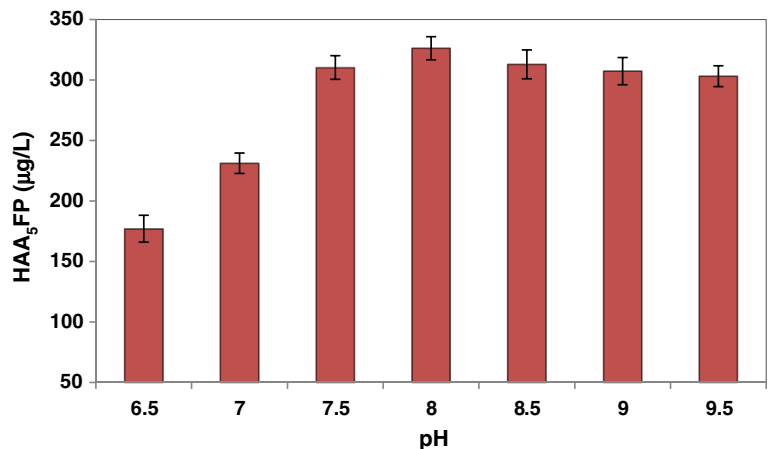
Seasonal variations of the HAA₅FP

Figure 6 presents the seasonal variation in the HAA₅ formation potential in the Karoon River water. For all of the water samples studied, the average highest HAA₅ concentrations were observed in the spring and fall seasons, while the lowest HAA₅ concentrations were observed in the summer season. Vedat et al. (2008) also obtained the highest average HAA₅ concentrations in the spring and fall. It was concluded that the seasonal variations in the DBPs were related to the changes in the NOM quantity and quality of the water sources. As for

THMs, HAA₅ are produced as a result of reactions between chlorine and the organic matter. A higher DOC level is thus likely to produce more HAA₅. The DOC/TOC ratio is shown in Fig. 7, and the majority of the TOC was converted into DOC in the fall (89 %) and spring (86 %) seasons, which may account for why the HAA₅ levels were highest during the fall and spring seasons.

These observations indicate a shift, not only in the quantity but also in the composition of the NOM following precipitation and suggest the presence of runoff humic substances leached from the upper soil layer (Volk et al. 2005). Hydrology and soil affect the NOM. The hydrologic conditions define the flow paths that the water takes in transporting the DOC to surface water resources such as lakes and rivers and where the water interacts with soil horizons of various mineral and inorganic properties (Aiken and Cotsaris 1995). In other

Fig. 8 The effect of water's pH on the HAA₅FP (reaction time 60 h, chlorine dose 10 mg/L, and TOC content 4.5 mg/L)



words, the UV_{254} measurement is a reasonable surrogate for the DOC value, not only in natural waters but also in other environments such as sediment pore waters (Deflandre and Gagne 2001; Volk et al. 2005; Tanita and Kimberly 2005). Recently, in other studies (Bond et al. 2009), it has been reported that the UV_{254} measurement is not a good surrogate for the DOC in terms of HAA formation. However, Volk et al. (2005) proposed that the sources of the DOC and their quality change with hydrology.

The formation potential of the HAA₅ species in the chlorinated water from the Karoon River is also shown in Fig. 6. As illustrated in Fig. 6, the major HAA₅ species were TCAA and DCAA. DBAA in amounts between 5.01 and 9.21 $\mu\text{g/L}$ of were formed in each of the seasons; therefore, DBAA had the lowest level of the HAA₅ species. This trend is may be due to the moderate level of bromide ions and the high initial chlorine dose (See Table 1, average bromide ions 142.5 $\mu\text{g/L}$).

The effects of pH

Figure 8 shows the effect of the initial water pH (6.5–9.5) on the HAA₅FP in the raw water of the Karoon River. After a reaction time of 60 h, the values of the HAA₅FP initially increased with the pH increase from 5.5 to 8. The HAA₅FP did not change with the increasing pH above 8, and the curve remained relatively flat. Three major reasons can account for this trend. First, the distribution of HOCl/OCl⁻ depends on the pH. HOCl, which is a more powerful oxidant than the hypochlorite ion (OCl⁻), is predominant at low pH values. Second, the organic charge and reactivity are dependent on the pH. Finally, the formation of individual DBPs can be affected by the pH (Hua and Reckhow 2007). Another probable reason is that these organic compounds have many functional groups, especially acetyl groups, that are active in the high pH range and react with chlorine, which agrees with the results from other research (Bixiong et al. 2009). However, as Platikanov et al. (2010) have noted, the pH would affect the equilibrium of the reaction and the effects of the pH on the chlorination process must be explained simultaneously by the deprotonation of the hypochlorite and/or the organic compounds that may change the reaction kinetics.

Conclusions

This study elucidated that the HAA₅FP is influenced by many water quality factors including the TOC, water temperature, chlorine content, pH, and seasonal variations. The chlorine dose has a functional relationship with the formation potential of the HAA₅, and the HAA₅FP displays a seasonal variation with the variation of the TOC content. The reactivity of the organic matter has shown some variation throughout the year, with the lowest reactivity (HAA₅FP) during the winter, increasing during the fall and usually reaching a maximum during the spring season. On the other hand, an increase in the DOC concentrations was observed in the fall and spring seasons. For all of the experiments, the HAA₅FP values were greater than the MCL of the HAA₅ (60 $\mu\text{g/L}$); therefore, this issue is very critical for the water treatment plant near the Karoon River. Thus, to meet the EPA standards for plants treating the Karoon River water, removing the NOM from the raw water before the chlorination unit or removing the HAA₅ after chlorination is imperative.

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