

## Formation potential of trihalomethanes (THMs) in blended water treated with chlorine

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### ABSTRACT

This study was conducted in the laboratory to assess the formation potential of trihalomethanes (THMs) in blended water under various treatment conditions. Three batches of water samples prepared by mixing desalinated (product) water and ground brackish water with three different proportions (i.e. 1:2, 1:5 and 1:10 – brackish:product water) were treated with three concentration levels of calcium hypochlorite and collected after 24 and 48 h. Other treatment runs were conducted under three different temperatures of 25, 35 and 45 °C. Results of the study indicated that brominated THMs (i.e. bromoform ( $\text{CHBr}_3$ ) and dibromochloromethane ( $\text{CHClBr}_2$ )) were the dominant components of the THMs formed in blended water. Results also showed that the total THMs (TTHMs) levels decreased as the portion of product water in the blended samples increased from 2 to 10. Results revealed that bromoform levels decreased and chloroform increased as the product portion increased. In this study, the TTHMs slightly increased as the chlorine dose increased from 1 to 5 ppm and as high as 175 ppb of TTHMs formed when the temperature of the water increased from 25 to 45 °C.

**Key words** | bromoform, chlorination, desalination, disinfection by-products (DBPs), trihalomethanes (THMs), water

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### INTRODUCTION

Saudi Arabia is located in an arid region and suffers from scarcity of fresh water sources and limited rainfall rates. Therefore, a major source of drinking water in Saudi Arabia originates from seawater desalination. Several multi-stage flash distillation (MSF) and reverse osmosis (RO) desalination plants along the coast of the Red Sea and Arabian Gulf supply more than 70% of municipal water in the Kingdom which is considered as the world's largest producer of desalinated water (Cotruvo *et al.* 2010). The distillates from desalination plants are usually blended with adequate amounts of brackish in order to enhance the mineral contents. Blending is also based on the demand-supply balance and this may lead to a change in the quality of the blended water. Before distribution to consumers, blended water is usually disinfected by chlorination through the addition of certain calcium hypochlorite concentrations in order to maintain a chlorine residual

of about 0.5 ppm. Unfortunately, the chlorination process may lead to the formation of harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) (Simpson & Hayes 1998; Chang *et al.* 2000, 2001; von Gunten *et al.* 2001; Nissinen *et al.* 2002; Anand *et al.* 2005; Ates *et al.* 2007; Hua & Reckhow 2007; Goslan *et al.* 2009).

Epidemiological studies have suggested a possible link between chlorination and chlorination by-products and an excess risk of bladder and rectal cancer (Clark *et al.* 1986; Melnick *et al.* 2007; Wang *et al.* 2007; Hamidin *et al.* 2008; Hrudey 2009). Because of the health effects associated with exposure to DBPs, many countries as well as the World Health Organization (WHO) have set regulations and/or guidelines on acceptable levels of DBPs in water. In 1979, the United States EPA initiated a regulatory Standard of 100 µg/L for THMs, under the 'Safe Drinking Water Act'. Currently, under Stage 1 of

the 'Disinfectant/Disinfection By-Product (D/DBP) Rule', this Standard has been reduced to 80 µg/L (EPA 2006).

In recent years, extensive research has been conducted in many parts of the world on emerging DBPs of health and regulatory issues (Sirivedhin & Gray 2005; Kim 2008; Roccaro *et al.* 2008; Bougeard *et al.* 2010). For example, Wei *et al.* (2010) assessed the spatial and temporal levels of disinfection by-products in drinking water distribution systems in Beijing, China. Results of their study showed that the levels of DBPs in drinking water varied with different water sources and followed the order: surface water source > mixture water source > ground water source. In another study, Hu *et al.* (1999) investigated the formation of by-products by ozonation followed by chlorination. Their study showed that chloroform, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the main constituents of THMs and HAAs, respectively.

A study conducted by Mayan Kutty *et al.* (1995) for monitoring the organic compounds in desalinated water samples in Al-Jubail, Al-Khobar and Al-Khafji desalination plants did not indicate the presence of any toxic chemicals in significant concentrations. Fayad & Tawabini (1991) conducted a survey of Saudi Arabian Drinking Water for THMs and found no chloroform formation in drinking water samples in the country's distribution network. Al-Mudhaf *et al.* (2009) also investigated the household drinking water samples, which were composed of water from desalination plants and blended with 5–10% brackish water to make it potable. Their study revealed that in addition to the four common THMs species, between one and six of the nine compounds (dibromomethane (DBM), 1,2-dichloropropane (DCP), toluene, 1,2,3- and 1,2,4-trichlorobenzene (TCB), naphthalene, total xylenes, benzene and 1,2-dibromo-3-chloropropane (DBCP)) were found with detection frequencies ranging from 0.2% for 1,2-DBCP to 91.3% for DBM. Tawabini *et al.* (1987) showed that there was an increase in the formation of THMs with an increase in chlorine dosage in distilled water (obtained from synthetic seawater) blended with ground water. Shams El Din *et al.* (1991) investigated the contribution to the problem of THMs formation from the Arabian Gulf Water. They found that chlorinated clean seawater contains bromoform (BF), dibromochloromethane (DBCM), di chlorobromomethane (DCBM) and

chloroform (CF). They found that bromoform makes 95% of the THMs.

In general, little work has been conducted to link the effect of blending process on the formation potential of THMs in water samples prepared by blending desalinated water with raw groundwater. This study aims to assess the extent of THMs formation under various conditions of blending ratios, chlorine dosages and reaction time as well as temperature.

## MATERIALS AND METHODS

Synthetic water samples were prepared in the laboratory by mixing desalinated and raw brackish samples. Desalinated (product) water samples were obtained from Al-Jubail MSF Desalination Plant located in Jubail City in the Eastern Province of Saudi Arabia along the coast of the Arabian Gulf and operated by the Saline Water Conversion Corporation (SWCC). While the raw brackish samples were obtained from a local well located within the Jubail area and extracted from a depth of about 150 m, different proportions of product and brackish were mixed to produce drinking water samples. The main quality parameters of the original seawater, groundwater (brackish) and distilled (product) water before blending are shown in Table 1, while the quality of blended water samples is described in Table 2.

**Table 1** | Quality parameters of seawater, product and brackish water

Parameter	Seawater	Product water	Brackish water
pH	8.16	5.2	7.4
TDS (ppm)	44,300	16	2,550
Conductivity (µS/m)	61,500	8	3,850
TSS (ppm)	420	4	80
Total hardness (ppm as CaCO <sub>3</sub> )	6,948	<5	201
Alkalinity (ppm as CaCO <sub>3</sub> )	124	<5	165
Bicarbonate (ppm as CaCO <sub>3</sub> )	151	<5	201
Chloride (ppm)	23,625	1.5	880
Bromide (Br <sup>-</sup> ) (ppm)	116	0.014	4
TOC (ppm)	1.34	0.22	0.18

**Table 2** | Analysis results of the blended water samples

Blending ratio (R)	Product (mL)	Brackish (mL)	Total volume (mL)	pH	TDS (ppm)	TOC (ppm)	Br <sup>-</sup> (ppm)
1:2	150	75	225	7	680	0.085	0.71
1:5	200	40	240	7	435	0.070	0.24
1:10	250	25	275	7	208	0.062	0.083

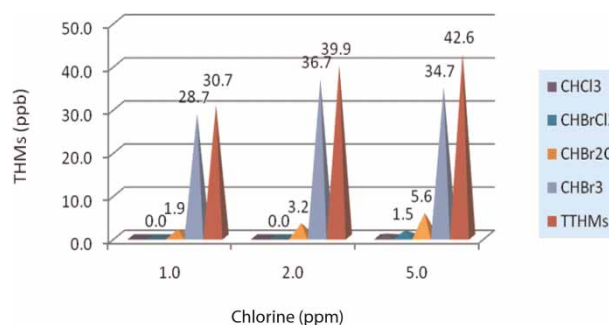
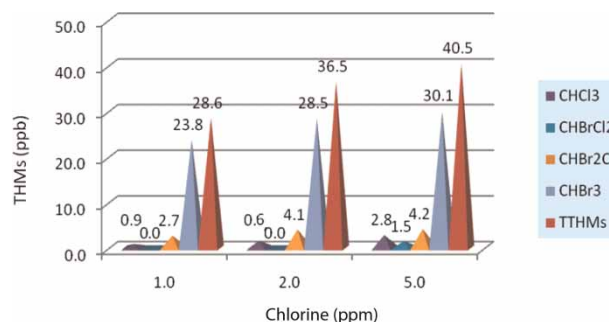
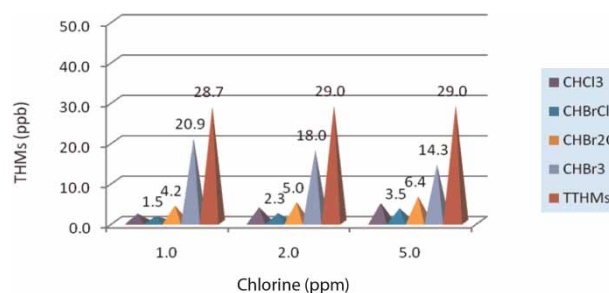
Standard test methods were used for the measurement of quality parameters as per the *Standard Methods for the Examination of Water and Wastewater* (AWWA 1998). Total organic carbon (TOC) in water samples was measured using the TOC analyser (TOC 5000 A) from Shimadzu, while the bromide ion (Br<sup>-</sup>) was measured using Dionex ICS-3000 RFIC ion chromatography (IC) system equipped conductivity detection system according to U.S. EPA Method 300.1 B.

In chlorination experiments, disinfection was carried out using a stock solution of 100 ppm calcium hypochlorite Ca(ClO)<sub>2</sub> which was purchased from Sigma. Fifty mL of blended water samples were disinfected by calcium hypochlorite at levels of 1, 2 and 5 ppm. Chlorine dosages and chlorine residual levels were measured by the *N,N'*-diethyl-*p*-phenylenediamine (DPD) method (AWWA 1998). Water samples were taken after 24 and 48 h in 15 mL glass vials capped with Teflon and sent to the laboratory to measure the THMs. Water samples were analysed by the Agilent 6890 GC/MS instrument equipped with a Purge and Trap unit (P&T) as per EPA method 501.2 Budde & Eichelberger (1979); Environmental Research Center (1979). The selected ion monitoring method (SIM) set at 83, 85, 127, 129, 171 and 173 was used for the analysis of THMs. The GC/MS system was calibrated with standard solutions of chloroform (CHCl<sub>3</sub>), dichlorobromomethane (CHCl<sub>2</sub>Br), dibromochloromethane (CHClBr<sub>2</sub>) and bromoform (CHBr<sub>3</sub>) which were purchased from Supelco.

## RESULTS AND DISCUSSION

### Type of THMs formed in the blended water samples

Results of analysis for DBPs formation after chlorinating blended water samples under different blending ratios and chlorine dosages are shown in Figures 1–3. The results

**Figure 1** | THMs levels (ppb) in blended water of 1:2 ratio, pH = 7, temperature = 25 °C after dosing with Cl<sub>2</sub> of 1, 2 and 5 ppm and reaction time = 24 h.**Figure 2** | THMs levels (ppb) in blended water of 1:5 ratio, pH = 7, temperature = 25 °C after dosing with Cl<sub>2</sub> of 1, 2, and 5 ppm and reaction time = 24 h.**Figure 3** | THMs levels (ppb) in blended water of 1:10 ratio, pH = 7, temperature = 25 °C after dosing with Cl<sub>2</sub> of 1, 2, and 5 ppm and reaction time = 24 h.

depicted in Figures 1–3 clearly indicate that THMs are formed under all treatment conditions for the different blended water samples. In addition, results showed that brominated THMs (i.e. bromoform ( $\text{CHBr}_3$ ) and dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ) were the dominant components of the THMs formed in all water formulations disinfected by chlorination. In fact, results show that bromoform represents more than 80% of the total THMs formed in the blended water samples regardless of the different mixing ratios or levels of chlorine dosage. On the other hand, chlorinated THMs (i.e. chloroform) was not detected in most of the samples. This is mainly due to the original high levels of bromide ion ( $\text{Br}^-$ ) in brackish which were also detected in the blended water samples in the range of 0.08–0.71 ppm, as shown in Table 1. The absence of chlorinated THMs can be attributed to the low levels of TOC levels which range from 0.06 to 0.08 ppm only. These results confirm the results obtained by other researchers (Sketchell *et al.* 1995; Kampioti & Stephanou 2002; von Gunten 2003; Imo *et al.* 2007).

One additional point to observe is that as the proportions of product water in the blended water samples increased compared to groundwater, less brominated and more chlorinated THMs are detected. It is observed that the bromoform level decreased and the chloroform level increased as the product proportion in the blended water increased from 2 to 10 as shown in Table 3. Again, this is attributed to the fact that the source of bromide ion which is responsible for forming brominated THMs is the brackish groundwater.

### Effect of blending ratio on THMs formation in the blended water samples

The effect of blending ratio (i.e. brackish:product water) levels on THMs formation in blended water samples

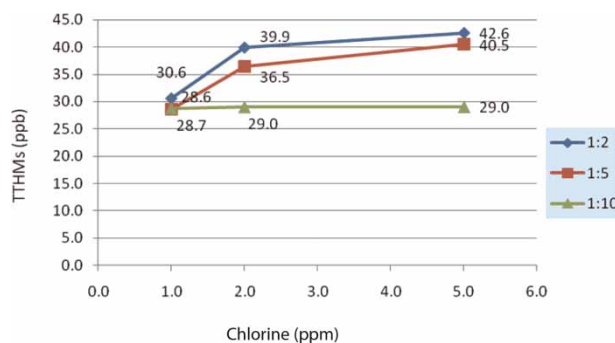
**Table 3** | Percentages of chloroform and bromoform in blended water samples at  $\text{Cl}_2 = 5$  ppm

Blending ratio	% Chloroform	% Bromoform
1:2	0	81
1:5	7	74
1:10	14	49

was also investigated in this study. Results are depicted in Figure 4. Results showed that higher THMs are formed in blended water samples with higher brackish (groundwater) portions. This can again be attributed to the fact that most of the THMs are formed in the form of brominated THMs and particularly bromoform due to the high levels of bromide ions in blended water samples with higher brackish portion. As shown in Figure 4, at a chlorine dosage of 5 ppm, TTHMs of 42.6 ppb were detected in 1:2 blended water samples compared with 29 ppb of TTHMs detected in 1:10 blended water samples. The effect of blending ratio was also observed at a chlorine dosage of 2 ppm but this diminishes at a chlorine dosage of 1 ppm.

### Effect of chlorine dosage on THMs formation in the blended water samples

The effect of initial chlorine dosage on the potential formation of THMs in blended water samples was also studied in this work. Different batches of blended water samples were treated with three levels of chlorine of 1, 2 and 5 ppm. The chlorine residuals recorded for these dosages were about 0.5, 1.4 and 3.4 ppm, respectively. It is clear from Figure 4 that, generally, THMs levels in blended water samples increases as the concentration of the chlorine dosage or the chlorine residual increases. For example, Figure 4 shows that TTHMs increased from 30.6 to 42.6 ppb as the chlorine dosage increases from 1 to 5 ppm. This result is expected due to the fact

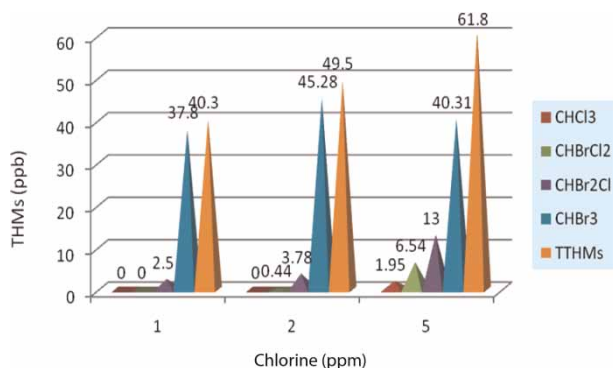


**Figure 4** | TTHMs levels (ppb) in blended waters of pH = 7, temperature = 25 °C after dosing with  $\text{Cl}_2$  and reaction time = 24 h.

that the chemical reaction by which THMs are formed depends on the chlorine concentration. However, it is noticed that even at much high levels of chlorine dosage of 5 ppm, which is much higher than the usual dosage, levels of THMs formed were between 29.0 and 42.6 ppb which are much lower than the maximum allowable limit of TTHMs of 80 ppb. This showed that the current practice of disinfecting blended water samples by chlorine is not expected to lead to the formation of harmful THMs if consumed within 24 h and water temperature does not exceed 25 °C.

### Effect of contact time on THMs formation in the blended water samples

The effect of contact time on the potential formation of THMs in blended water samples was also investigated in this study. Different batches of blended water samples were treated with three levels of chlorine of 1, 2 and 5 ppm. Samples were collected after 24 and 48 h to study the effect of contact time on the formation of THMs in blended water samples. The THMs levels measured in 1:2 blended water samples at room temperatures dosed with 1, 2 and 5 ppm of chlorine and collected at room temperature after 48 h are shown in Figure 5. By comparing the results in Figures 1 and 5, it is clear that contact time has a significant effect on the formation potential of THMs. For instance, total TTHMs concentration levels increased from 42.6 to 61.8 ppb when the contact time increased from 24 to 48 h, representing an increase of 31% of TTHMs. These results also confirm previous results by



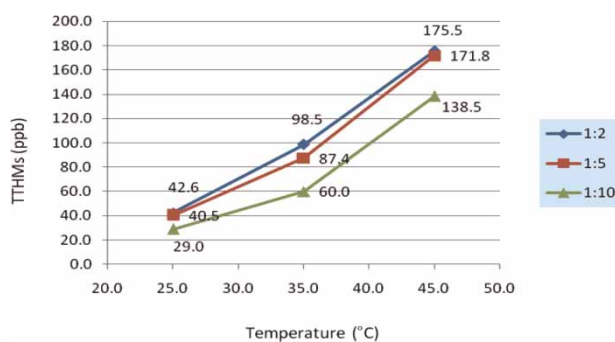
**Figure 5** | THMs levels (ppb) in blended water of 1:2 ratio, pH = 7, temperature = 25 °C after dosing with Cl<sub>2</sub> of 1, 2, and 5 ppm and reaction time = 48 h.

other researchers which show that the formation of DBPs is time dependent.

### Effect of temperature on THMs formed in the blended water samples

The effect of temperature on the potential formation of THMs in blended water samples was also investigated in this study. Different batches of blended water samples were treated with three levels of chlorine of 1, 2 and 5 ppm. Temperatures of blended water samples were set at three levels of 25, 35 and 45 °C using a water circulation bath. Samples were then collected after 24 h and analysed for THMs in blended water samples. Results of this part of the study are shown in Figure 6. The results in Figure 6 clearly indicate that temperature has a significant effect on the formation of THMs in blended water samples. For example, TTHMs levels increased from around 29 to 138.5 ppb when the temperature increased from 25 to 45 °C in water samples blended with 1:10 brackish to product water. Similarly, TTHMs increased from 40.5 to 171.8 ppb and from 42.6 to 175.5 ppb when the temperature increased from 25 to 35 °C for a blending ratio of 1:5 and 1:2, respectively.

The TTHMs levels formed at 45 °C in the three blending ratios dosed with 5 ppm chlorine is much higher than the USEPA maximum contaminant levels (MCLs) of TTHMs of 80 ppb. However, TTHMs levels were lower than MCLs for chlorine dosage of 25 °C. It should be noted that if the water is heated to a temperature of 35 °C and dosed with chlorine dosage of 5 ppm, TTHMs levels might exceed the



**Figure 6** | TTHMs levels (ppb) in blended waters of pH = 7, Cl<sub>2</sub> dose = 5 ppm at different temperatures and reaction time = 24 h.

MCLs of 80 ppb. However, water authorities do not usually disinfect the water with such high levels of chlorine.

## CONCLUSION

The study showed that chlorinating blended water samples will lead to the formation of THMs regardless of the blending ratio used to prepare these blends. Results showed that brominated THMs, and especially bromoform, are the dominant THMs formed due to the levels of bromide ion in the blended samples which varies according to the blending ratio. Chlorine dosage, contact time and temperature have a significant role in determining the extent of THMs formation in blended water samples. Based on the results of the study, it is highly recommended that the water authority carefully observe the disinfection of blended waters and avoid using high ratios of well waters in the blended drinking water samples. They also need to closely monitor the disinfection conditions when applying chlorine, including dosage and temperatures.

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