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CHLORINATION BYPRODUCTS IN DRINKING WATER PRODUCED FROM THERMAL DESALINATION IN UNITED ARAB EMIRATES

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Abstract. Oil activities in the Arabian Gulf can potentially affect the quality of the intake water available for coastal desalination plants. This paper addresses such situation by investigating the quality of intake water and desalinated water produced by a desalination plant located near a coastal industrial complex in United Arab Emirates (UAE). Analyses of the organic compounds on the intake seawater reported non-detected levels in most samples for the three tested organic groups; namely Polyaromatic Hydrocarbons (PAHs), Phenols, and Polychlorinated Biphenyls (PCBs). Trihalomethanes (THMs) and Haloacetic Acids (HAAs) were also tracked in the intake sea water, throughout the desalination processes, and in the final produced drinking water, to evaluate the undertaken pre- and post chlorination practices. The levels of considered Chlorination Byproducts (CBPs) were mostly found below the permissible international limits with few exceptions showing tangible levels of bromoform in the intake seawater and in the final produced drinking water as well. Lab-controlled experiments on the final produced distillate showed little contribution of its blending with small percentage of seawater upon the formation of trihalomethane and in particular, bromoform. Such results indicate that the organic precursors originated in the seawater are responsible for bromoform formation in the final distillate.

Keywords: bromoform, chlorination byproducts, desalination, drinking water, United Arab Emirates

1. Introduction

The presence of desalination plants along the coast of industrial areas in the oil-reach countries like United Arab Emirates prompts the need of investigating the possible contamination of drinking water with trace, yet hazardous organic compounds. This is particularly true given the fact that major chlorination is usually practiced at the plant's seawater intake to eliminate possible marine fouling inside the distillers and to kill jelly fishes and/or bulky aquatic species that may be drawn with the seawater entering the plant. Oil refineries, loading/unloading facilities, petrochemical industries, and single point mooring stations are among the various activities found in coastal areas and can potentially and adversely affect the quality of intake water used in desalination. Many of the organic substances released from such activities may pose threat to human health if not adequately removed by the desalination processes. It is therefore essential to track potential organic contaminants found in the coastal water and report their possible residual levels after passing the desalination process.

Even though the thermal distillation process splits most of the salts out of the seawater and de-mineralizes the water, some of the evaporated volatile organics may partially condense back into the final produced distillate. Post treatment for mineralization and post chlorination for disinfection may also contribute to the formation of other organic byproducts in the finished drinking water, some of which may pose risk if found with elevated levels. It is therefore necessary to assess the efficiency of thermal desalination processes in removing any organics entering the plant with seawater or formed during its travel or phase transformation throughout various thermal processes.

United Arab Emirates primarily relies on seawater thermal desalination as a first priority for drinking water resources. More than 95% of the total 330 MGD desalinated water produced nationwide comes from coastal thermal desalination processes. A thorough and careful study of the quality of drinking water produced from these coastal desalination plants is therefore essential. The objectives of this work are summarized in three points as follows:

1. Evaluate the quality of seawater at the intake of the desalination plant.
2. Assess the efficiency of thermal desalination processes in removing soluble organic compounds and CBPs precursors from the produced distillate and in eliminating the formation of hazardous organics, in particular the halogenated ones upon pre and post chlorination processes.
3. Assess the impact of ongoing re-mineralization practice of blending small percentages of seawater with the final distillate upon the formation of CBPs.

2. Relevant Studies

A great number of studies have been conducted to evaluate the disinfection byproducts in drinking water produced from surface and/or ground water. However, only few studies have addressed the topic in case of having the source of drinking water as seawater and the treatment process as thermal desalination. Most of these studies were conducted in the Arabian Gulf area since the Gulf countries heavily rely on desalination of seawater as their primary source of drinking water. A common finding of such studies is that bromoform was the main byproduct that forms upon chlorinating the bromide-rich seawater.

Shams *et al.* (1991) analyzed the seawater in Umm Al Nar desalination plant in Abu Dhabi, the Capital City of United Arab Emirates and examined its potential to form trihalomethane compounds after chlorination. The study showed that bromoform represented 95% of the formed THM in seawater and in the final distillate as well. The authors related the reason of high bromoform formation to the high bromide levels in seawater. The study also included laboratory experiments to confirm the bromoform formation at varying levels of bromide and Cl_2. Ali and Riley (1986) reported measured levels of bromoform ranging from 10 to 90 μg/l in the vicinity of various power/desalination plants in the Kuwaiti Coastal water. The presence of bromoform in marine water may adversely affect the embryonic and larval stages of marine organisms and the possibility of mimicking hormones released by marine organisms and thus interfere with the chemical communication system of these organisms causing disruption of their life cycle.

Another study (Elshorbagy *et al.*, 2000) has also identified the dominance of bromoform as CBPs in Abu Dhabi water distribution system known to receive a major potion of its drinking water from the same desalination plant mentioned above; Umm Al-Nar. The study modeled the propagation of THM species in water distribution systems by accounting for the kinetics of TTHM formation, kinetics of bromoform formation, and the general distribution of THM species formed at the source. The approach merged the site-specific quality trends with stoichiometric expressions based on an average representative bromine content factor (BIF).

Saeed *et al.* (1999) investigated the presence of halogenated volatile liquid hydrocarbons (HVLHs) in the vicinity of inlets and outlets of power/desalination plants in Kuwait. The results showed that THM compounds contributed the bulk of the total HVLHs of which bromoform constituted more than 87%. Cooling water discharges had significantly contributed to the formation of the detected HVLHs.

In another study conducted in Greece (Kampioti and Stephanou, 2002), the brominated DBPs were more abundant than their chlorinated homologues due to the high concentration of bromide in raw coastal water.

Wu *et al.* (2001) conducted a study that implicitly indicates that the thermal distillation may not totally inhibit the formation of halogenated DBPs. They investigated the effect of boiling and heating the drinking water upon the generation/destruction of DBPs. The experiments were conducted on three samples; DBP-spiked reagent water, municipal tap water, and synthetic water containing aquatic humic substances. The results show that chemical transformation occurs at elevated temperatures where large halogenated THMs and HAAs lead to formation of smaller chlorinated ones.

The authors have no knowledge of any study conducted to track individual synthetic organic compounds through out the desalination processes.

3. Application Site

Ruwais is an industrial complex located along the northern coast of the UAE at about 230 kilometers west of the Capital City, Abu Dhabi. The complex is sheltered by Bani Yas Island at the north west side, a large inter-tidal area at the east side, and Jabal Dhannah, a headland at the west side. The 5 m depth contour is located at about 2 km off the coast and a relatively deeper basin at the north (> 15 m) is extended from the offshore to the proximity of the coast. The coastal area hosts several industrial facilities such as oil refinery, petrochemical factory, sulfur production unit, and fertilizer-productions unit. Loading and unloading activities along the shore line as well as around three offshore single points of mooring are located in the coastal water along with a general utility thermal desalination plant.

The desalination plant at the Ruwais complex provides potable water for drinking water as well as for general plant consumption such as service utility water and firewater. The plant has five Multi Stage Flash (MSF) desalination units with a total production capacity of 64,000 m^3/day fresh water. The MSF principle is based upon raising the temperature so that the seawater flashes when subjected to a pressure drop in the first stage of the plant. The MSF operates from a positive pressure in the first stage to a high vacuum in the last stage. The distillate produced is further processed to drinking water to control the corrosion and algae growth. This is done by the addition of chemicals such as PO_4^{3-} and lime to re-mineralize the distillate and CO_2 to recarbonate and adjust the pH. In addition to these chemicals, the final distillate is blended with a small portion of seawater (0.2% mixing ratio or 2 liters of seawater is blended with each one m^3 of distillate). The concentrated brine (blowdown) is then discharged into the sea.

4. Sampling and Analytical Methods

An intensive sampling program was conducted in the application site on various onshore and offshore locations. The onshore locations include the desalination plant intake and effluent in addition to samples taken after different thermal desalination stages inside two units of the plant itself; namely unit 1 (MSF1) and unit 5 (MSF5). Table I lists the considered samples along with their description. Figure 1 shows a schematic description of the sampled system showing the locations of different samples. Two sampling locations exist at the plantś intake, eight locations inside MSF1, five inside MSF5, four in the plant effluent and drinking storage area, and one in the brine blowdown. While seven sampling trips were conducted over one full year (2003) covering most sampling locations, locations inside unit 5 (S11 to S15) were sampled in the last two trips only to evaluate its performance in comparison with unit 1.

Samples were taken in all locations for analyses of individual organic compounds of three groups; PAHs, Phenols, and PCBs. In addition, other samples were taken from the desalinated streams inside the desalination plant and after post-treatment for the analyses of the most common and usually regulated DBPs, namely the four trihalomethanes and the five haloacetic acids. Due to the unavailability of sampling ports in the condensate rejection stream, it was not possible for the current study to evaluate the levels of byproducts generated in the thermal process and vented outside the process. However, other studies showed that such stream usually removes most of the generated byproducts from the system. Shams *et al.* (1991) reported significant levels of brominated THM compounds in the ejector system

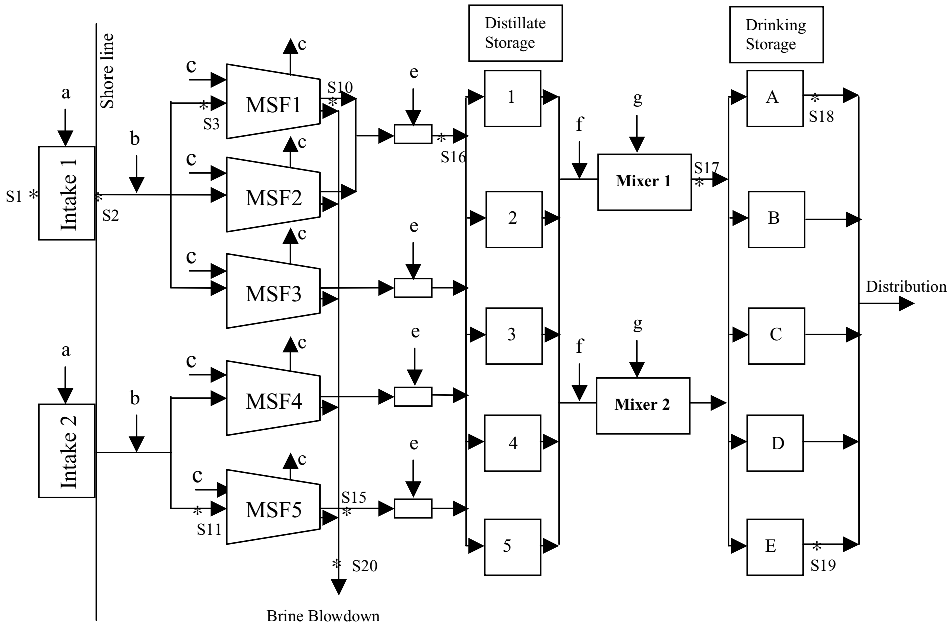
TABLE I
Location and description of sampling points

Sample No.	Description
S1	Intake before chlorination
S2	Intake after chlorination
S3	Makeup seawater of MS1
S4	Feed to brine heater in MSF1 (after the heat exchanger)
S5	Inside MSF1, after stage (1)
S6	Inside MSF1, after stage (2) NaOH/PO_4^{3-}
S7	Inside MSF1, after stage (3)
S8	Inside MSF1, after stage (7)
S9	Inside MSF1, after stage (10)
S10	Final distillate of MSF1
S11	Makeup seawater of MS5
S12	Inside MSF5, after stage (3)
S13	Inside MSF5, after stage (7)
S14	Inside MSF5, after stage (10)
S15	Final distillate of MSF5
S16	Final distillate after adding
S17	Influent of drinking storages
S18	Effluent of drinking storage A
S19	Effluent of drinking storage E
S20	Brine Blowdown

(0.285 mg/L, 1.60 mg/L, and 15.754 mg/L for dichlorobromoform, dibromochloroform, and bromoform, respectively).

In addition to regular water quality measurements, the conducted organic analyses included Phenols as a potential petroleum-related pollutant in addition to PAHs and PCBs.

TOC and DOC measurements were measured using SHIMADTZU TOC5000 analyzer that employs IR combustion method. The DOC samples were obtained after successive filtration of the raw samples with micro-pore glass filter papers undergone long soaking in deionized water. Analysis of PAHs, Phenols, and PCBs were analyzed according to relevant standard methods (APHA, 1995). PAHs determination involved an extraction of a known volume of water using methylene chloride that is carefully removed later by evaporation. Sample extracts are cleaned, if necessary, via Solid Phase Extraction (SPE) using PAH SPE columns. The PAH components in the extract are detected and determined by HPLC using ultraviolet fluorescence and photodiode array detectors simultaneously. For phenol determination, the samples were extracted using hexane prior to analysis. The target phenols



a	chlorine dosing	b	anti-scale/anti-foam dosing
c	steam feed	d	condensate rejection
e	NaOH/PO$_4^{3-}$ dosing	f	seawater blending
g	chemical dosing (Cl$_2$, Lime, CO$_2$, PO$_4^{3-}$)	Si	sample i

Figure 1. A simplified schematic of the desalination plant and sampling locations (Note: S4 to S9 are inside MSF1 and S12 to S14 are inside MSF5).

were derivatized with pentafluorobenzylbromide (PFBBr) and analyzed by gas chromatography. PCBs were extracted from a known volume using an appropriate matrix specific sample extraction technique. Extracts were subjected to sulfuric acid/potassium permanganate cleanup and the cleaned extract was analyzed by gas chromatography on a narrow-bore fused silica capillary column and Electron Capture Detector (GC/ECD).

5. Intake Water Quality

The desalination plant intake is located inside the semi-enclosed coastal area where the depth varies from 2.0 to 3.0 m depending on the tidal conditions. A relevant hydrodynamic study (Azam *et al.*, 2005) indicated that the prevailing onshore water currents are somewhat low and the water dynamics and circulation are generally weak and promotes stagnant conditions.

The feed water intake consists of a screening chamber and distribution channel fitted with continuous dosing of chlorine besides shock dosing at predetermined intervals. The feed is then pumped to the heat rejection section of the desalination train. A number of halogenated organics can potentially form at the intake point in association with such chlorination process in the presence of natural and/or synthetic organic precursors. Therefore, monitoring of inorganic and organic conditions at the intake point before chlorination was conducted for overall quality evaluation and for evaluating the presence of potential CBPs precursors.

Table II lists some physical characteristics and inorganic analyses of the seawater at the intake location of the desalination plant obtained from different site visits. All analyses were carried out on samples taken from a constant depth of 1.0 m below the surface except for the dissolved oxygen; that was reported onsite at about 2.0 m depth. To check the variability of conducted analyses over the depth, few selected analyses and onsite measurements (pH, DO, and Temp.) were earlier carried out at different depths during the summer time. The results of such analyses showed intangible depth variation so that sampling from one depth was found adequate and representative.

The table shows that DO magnitudes were relatively higher in the winter months with values mounting to 6.75 mg/L than the warm summer months with values dropping to as low as 5.45 mg/L. This can be attributed to the higher saturation water capacity to dissolve oxygen and other gases and the lower volatility of such gases at lower temperatures. pH values experienced slight variation with time with an average annual value of 8.3. The magnitudes of nitrogenous ions including ammonium, nitrites, and nitrates were slightly higher in summer time than in winter with again exceptional high levels reported during the month of January. The levels of these compounds, especially the nitrates, were generally high if compared with their counterpart levels reported in other areas of the Arabian Gulf. This may be related to the effluents of fertilizer and petrochemical plants located near the intake location along the same shoreline. In terms of the salinity of the intake seawater, it is noticed that it was relatively higher in the winter months than it is in the summer months due to the high winter evaporation rates associated with strong prevailing winds. The higher winter evaporation has been attributed to a well-known strong north western wind known as Shamal and has been documented by several past and recent studies (Perrone, 1979; Elshorbagy *et al*., 2006). The salinity levels in Ruwais area has been reported to be generally higher than other onshore coastal areas in the UAE or than offshore deeper water as well (Elshorbagy *et al*., 2005).

Besides the intake water analyses listed in Table II, a selected number of trace and heavy metals were analyzed on September of 2002 to represent the summer conditions and on March of 2003 to represent the winter conditions. The results are listed in Table III where slight variation exists between the two seasons. The non-detected levels of the hazardous elements; chromium, nickel, lead, copper and mercury, eliminated the need of their measurements in March visit.

Organic analyses conducted on the intake water (location S1) included TOC, DOC, SUVA, TPH, THMs, HAA5, PAHs, Phenols, and PCBs. Table IV lists the analytical results for TOC, DOC, SUVA, TPH, THMs, and HAA5 while Tables V–VII

TABLE II

Physical and inorganic analysis for intake seawater at different site visits

Date	Temp. (°C)	DO (mg/L)	pH	NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	Cl^- (mg/L)	P as PO_4^{3-} (mg/L)	Br^- (mg/L)	Salinity psu[a]
18/03/2002	27.84	NM[b]	8.4	0.29	0.004	0.6	NM	NM	NM	45.84
16/06/2002	33.65	5.45	8.4	0.26	0.012	1.0	24950	0.082	NM	45.79
30/07/2002	33.85	5.85	8.3	0.18	0.011	0.8	26000	0.078	91	45.65
17/09/2002	33.75	5.95	8.3	0.13	0.008	1.1	24600	0.092	87	45.53
05/11/2002	24.65	6.15	8.3	0.09	0.006	0.1	23000	0.015	90	46.07
08/01/2003	22.34	6.75	8.2	0.12	0.057	0.2	36000	0.130	88	46.15
15/03/2003	27.50	6.68	8.2	0.07	0.005	0.7	32500	0.060	NM	45.92
Average	29.06	6.14	8.3	0.16	0.015	0.64	27841.7	0.076	89.00	45.89
Std. dev.	4.744	0.502	0.082	0.084	0.019	0.378	5176.1	0.038	1.826	0.245

[a] Practical Salinity Unit (parts per thousand parts)

[b] Not measured

TABLE III
Levels of selected heavy metals at the intake seawater (mg/L)

Season	Na	K	Ca	Mg	Al	Sr	Cr	Ni	Pb	Co	Hg
Summer	12640	520	468	1469	NM	10.6	ND	ND	ND	ND	ND[a]
Winter	14200	523	413	1550	0.008	5.8	NM	NM	NM	NM	NM[b]

[a] Not detected
[b] Not measured

TABLE IV
Surrogate Organic parameters and CBPs for intake seawater

Parameter	Range of all visits	September 02
TOC (mg/L)	5.3–9.0	18.13
DOC (mg/L)	1.5–5.9	6.45
Absorb. at 254 nm NM	0.05–0.19	NM[a]
SUVA (L/mg)	3.5–4.3	NM
TPH (mg/L)	0.9–3.3	9.60
THMs (μg/L)		
Chloroform	<0.20	ND[b]
Bromodichloromethane	<0.20	ND
Dibromochloromethane	<0.20	ND
Bromoform	<0.2–2.5	1.38
Monochloroacetic Acid	<1.0–3.5	1.7
HAA5 (μg/L)		
Monobromoacetic Acid	<1.0	ND[c]
Dichloroacetic Acid	<1.0	ND
Trichloroacetic Acid	<1.0	ND
Dibromoacetic Acid	<1.0	ND

[a] Not measured
[b] Not detected with THM detection limit of o.1 μg/l
[c] Not detected with HAA5 detection limit of 1.0 μg/l

list the individual components of Phenols, PAHs, and PCBs, respectively. The ranges reported in Tables IV and V (except HAA5) were based on five field visits conducted during years 2002 and 2003. The range of HAA5 was based on three visits conducted in year 2002 where most of the analyzed samples showed lower levels than the equipment quantification limit of 1.0 μg/L. The ranges of Phenols and PCBS (Tables VI and VII) were based on two field visits conducted in year 2003.

High ranges of TOC and DOC were reported in the intake water (5.3–9.0 mg/L for TOC and 1.5–5.9 mg/L for DOC). The high reported levels may be attributed to the shallow depth at the intake location that promotes sediment suspension and to the intensive loading/unloading oil activities taking place in the nearby coastal water

TABLE V
Phenols for intake seawater (mg/L)

Phenol	Range
m-Cresol	0.15–0.22
o-Cresol	ND
p-Cresol	0.1–0.2
2,4-Dimethylphenol	ND
o-Chlorophenol	ND
2,6-Dichlorophenol	ND-0.05
4-chloro-3Cresol	ND
2,4-Dichlorophenol	ND
o-Nitrophenol	ND
2,4,6-Trichlorophenol	ND
2,4,5-Trichlorophenol	ND
p-Nitrophenol	ND
2,3,4,6-Tetrachlorophenol	ND
Pentachlorophenol	ND
2,4-Dinitrophenol	ND
2-Methyl-4,6dinitrophenol	ND
Dinoseb	ND

*ND: Not detected with Phenol detection limit of 0.01 mg/L

that can eventually contribute to accidental oil spills and hydrocarbon dispersion in the water column. Exceptionally high values were reported for the samples collected during September 2003 for TOC and DOC (18.1 and 6.5 mg/L) and were not included in the reported range. Other organic contaminants recorded high levels in that day as will be discussed later.

The dissolved organic carbons of natural aquatic ecosystem can be generally originated from two sources; [1] allochthonous entering the system from terrestrial sources, and [2] autochthonous derived from biota (e.g, algae, bacteria, and macrophytes). The chemical characteristics of the DOC are influenced by the source materials as well as the biogeochemical processes prevailing in the aquatic system. The later processes include degradation of particulate organic matter by heterotrophic microbial activity, transport of particulate organic carbon 'POC' to the sediments, remobilization of DOC from the sediments, and photo degradation by incident ultraviolet (UV) light. In industrial coastal waters like the studied application site, petroleum contaminants may also potentially contribute to the dissolved organic carbon.

Specific Ultraviolet Absorbance (SUVA) is defined as the UV absorbance of a given sample determined at 254 nm and divided by the DOC concentration (mg/L) of the solution. Chin, Aiken, and O'Loughin (1994) noted a strong correlation between

TABLE VI
PAHs for intake seawater (μg/l)

PAH	Range of all visits	September 02
Naphthalene	<0.1	110
Acenaphthylene	<0.1	ND
Acenaphthene	<0.1	ND
Flourene	<0.1	ND
Phenanthrene	<0.1	110
Anthracene	<0.1	20
Flouranthene	<0.1	70
Pyrene	<0.1	20
Benzo(a) anthracene	<0.1	20
Chrysene	<0.1	ND
Benzo(b) flouranthene	<0.1	ND
Benzo(K) flouranthene	<0.1	ND
Benzo(a) pyrene	<0.1	770
Dibenzo(a,h) anthracene	<0.1	ND
Benzo (g,h,i) perylene	<0.1	ND
Indeno (1,2,3-cd) pyrene	ND	ND

*ND: Not detected with PAH detection limit of 0.08 μg/l

SUVA and the aromatic-carbon contents of a large number of fulvic acids. SUVA is, therefore, a good predictor of the aromatic-carbon content of water's natural organic matter (NOM). By assessing the SUVA of intake water, one can assess the potential of seawater natural organic precursors to form disinfection byproducts (DBPs) upon chlorination. High levels of SUVA reflect high potential of DBP formation. The calculated values of SUVA obtained from the measurements conducted for two trips in year 2002, were in the range of 3.5 to 4.3 L/mg. According to empirical relation developed by Reckhow, Singer, and Malcolm (1990), this SUVA range corresponds to about 10–20% of the total DOC as aromatic carbon originated from NOM (fulvic acids, humic acids, and transphilic acids) and can contribute to the formation of halogenated hydrocarbons.

The reported TPH varied over the sampled year between 0.91 to 3.3 mg/L with an exceptionally high level of 9.6 mg/L on September 2002. A few PAH components did also show extremely elevated levels on that day (110 ppb for Naphthalene, 110 ppb for Phenanthrene, 20 ppb for Anthracene, 70 ppb for Flouranthene, 20 ppb for Pyrenem 20 ppb for Benzo[a]anthracene, and 770 ppb for Benzo[a]pyrene). It is not clear the reason behind the large contamination reported on that day, but the likelihood of accidental oil spill related to the ongoing loading/unloading activities may have potentially attributed to such high levels. None of the sixteen examined PAHs showed values higher than the detection limit (0.1 ppb) in all other visits.

TABLE VII
PCBs for intake seawater (μg/l)

PCB	Range
PCB 8 (2,4′-dichlorobiphenyl)	NC-0.1
PCB 18 (2,2′,5-Trichlorobiphenyl)	ND
PCB 28 (2,4,4′-Trichlorobiphenyl)	ND
PCB 52 (2,2′,4,4′-Tetrachlorbiphenyl)	ND
PCB 44 (2,2′,3,5′-Tetrachlorbiphenyl)	ND
PCB 66 (2,3′,4,4′-Tetrachlorbiphenyl)	ND
PCB 101(2,2′,4,5′,5-Pentachlorbiphenyl)	ND
PCB 77 (3,3′,4,4′-Tetrachlorbiphenyl)	ND
PCB 118 (2,3′4,4′,5-Pentachlorobiphenyl)	ND
PCB 153 (2,2′,4,4′,5,5′-hexachlorbiphenyl)	ND
PCB 105 (2,3,3′,4,4′-Pentachlorbiphenyl)	ND
PCB 138 (2,2′,3,4,4′,5′-hexachlorbiphenyl)	ND
PCB 126 (3,3′,4,4′,5′-Pentachlorbiphenyl)	ND
PCB 187 (2,2′,3,4′,5,5′,6-heptachlorbiphenyl)	ND
PCB 128 (2,2′,3,3′,4,4′ hexachlorbiphenyl)	ND
PCB 180 (2,2′,3,4,4′,5,5′-heptachlorbiphenyl)	0.1–0.31
PCB 170 (2,2′,3,3′,4,4′,5-heptachlorbiphenyl)	ND
PCB 195 (2,2′,3,3′,4,4′,5,6-Octaachlorbiphenyl)	ND
PCB 206 (2,2′,3,3′,4,4′,5,5′,6-nonachlorbiphenyl)	ND
PCB 209 (2,2′,3,3′,4,4′,5,5′,6,6′-decachlorbiphenyl)	ND

[*] ND: Not detected with PCB detection limit of 0.03 μg/l

In terms of DBPs measured in the intake, most of the considered individual components showed levels below the detection limit except for the bromoform ($<$0.2–2.5 ppb) and the chloroacetic acid ($<$1.0–3.5 ppb). It should be noted that the sampled intake point is located before chlorination and therefore the DBPs are as low as expected.

6. Organic Analyses Inside the Desalination Plant

Results of selected organic analyses inside and downstream the desalination plant (S2 to S20) are given in Table VIII. These include TOC, DOC, SUVA, THM and HAAs analyses given in ranges. Few observations can be made about these results. First, the levels of most individual organic compounds were extremely low and in many cases non detected except for bromform in few samples. The reported bromoform in the samples located inside the desalination process and in the final distillate before post chlorination (S16) indicated that the thermal desalination

TABLE VIII
Ranges of selected organic analyses at other locations

Sample	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20
TOC (mg/L)	2.22–7.23	2.10–6.22	0.31–5.82	1.11–3.12	1.30– 3.0	0.24–1.74	0.60–2.70	0.40–2.60	0.30–1.80	4.20–8.00	0.70–0.90	0.40–0.55	0.47–0.63	0.14–0.24	0.63–2.14	2.13–5.12	1.23–4.82	1.63–3.12	4.03–7.14
DOC (mg/L)	0.92–3.23	1.51–2.82	0.13–2.24	0.83–3.02	0.52–1.73	0.10–0.85	0.16–0.25	0.04–0.80	0.04–0.44	1.21–2.23	0.25–0.45	0.09–0.25	0.21–0.31	0.05–0.12	0.24–0.84	0.56–1.10	0.76–2.14	0.63–1.02	2.24–2.72
UVA at 254 nm	.017–.139	.036–.115	.001–.064	.000–.072	.000–.031	.000–.008	.000–.004	.000–.011	.000–.019	.018–.092	.000–.020	.000–.006	.000–.006	.000–.001	.004–.024	.000–.016	.000–.028	.000–.019	.440–.729
SUVA (L/mg)	1.90–4.35	2.41–4.12	1.29–3.78	0.00–2.41	0.00–1.83	0.00–0.95	0.00–1.62	0.00–1.38	0.00–4.42	1.52–4.19	0.00–4.46	0.00–2.33	0.00–1.92	0.00–1.01	1.83–2.83	0.00–1.42	0.00–1.30	0.00–1.93	20.00–27.00
THM (μg/L)																			
Chloroform	<0.2– 1.36	<0.2– 0.41	<0.2- 0.63	<0.2–1.02	<0.2–0.51	<0.2	<0.2– 0.28	<0.2–0.22	<0.2–0.29	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2–0.65	<0.2	<0.2–2.48	<0.2–0.23	<0.2–0.23
Bromodichloromethane	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2–0.27	<0.2–0.32	<0.2
Dibromochloromethane	<0.2–0.45	<0.2–3.64	<0.2–0.21	<0.2	<0.2– 0.42	<0.2–0.36	<0.2	<0.2–0.23	<0.2–0.73	<0.2– 0.71	<0.2	<0.2	<0.2	<0.2	<0.2–0.52	<0.2	<0.2–4.05	<0.2–4.93	<0.2
Bromoform	0.3–23.0	2.1–89.0	<0.2–10.4	<0.2– 2.5	3.4–28.3	<0.2–26.9	<0.2– 8.0	<0.2–14.7	1.1–41.2	5.0–40.5	<0.2–0.6	<0.2–1.8	<0.2	<0.2–1.8	0.3–26.4	<0.2– 8.7	3.4–27.6	3.2–61.2	<0.2–0.8
HAA5 (μg/L)																			
Monochloro-acetic Acid	<1.0–1.1	<1.0– 3.6	<1.0– 1.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	NM	NM	NM	NM	NM	<1.0	<1.0	<1.0	<1.0	<1.0–3.6
Monobromo-acetic Acid	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	NM	NM	NM	NM	NM	<1.0	<1.0	<1.0	<1.0	<1.0
Dichloro-acetic Acid	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	NM	NN	NM	NM	NM	<1.0	<1.0	<1.0	<1.0	<1.0
Trichloro-acetic Acid	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	NM	NM	NM	NM	NM	<1.0	<1.0	<1.0	<1.0	<1.0
Dibromo-acetic Acid	<1.0–13.4	4.9–9.0	<1.0–9.8	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	NM	NM	NM	NM	NM	<1.0	<1.0– 1.7	<1.0– 2.9	<1.0– 5.7	<1.0–11.6

process did not completely remove the bromoform originally found in the source seawater or formed after chlorination at the intake point. This was also evidenced from the levels of TOC, DOC, and SUVA reported inside the desalination process, even though with trace levels. Second, the levels of various measurements for different sampling visits were fluctuating within a small figure during some times (not quantifiable by the employed analytical method) and a rather tangible figure in other times. For example, the level of dibromoacetic acid was reported high at some locations (S2, S3 and S4) for two sampling visits while they were always below the quantification limit in all other trips. The third observation was the levels of TOC, DOC, and SUVA inside the desalination process and after different distillation stages were in general low for locations S5 to S10 in unit 1 and S12 to S15 in unit 5. However, they were relatively lower in unit 5 than in unit 1 indicating higher efficiency of unit 5 in removing the organic residuals from the produced distillate. Finally, the levels of TOC, DOC, and THM components (especially the bromoform) along the sequenced desalination stages were not following a specific trend in a given sampling visit and were somewhat erratic in its occurrence. This may be attributed to the random and erratic vaporization and condensation of these compounds inside the distillers knowing that only one ventilation stream is available for all stages. The temporal fluctuation of production rate and the time lag between the instances of collecting various samples, even though short, may also contribute to the reported variation.

The table shows that the intake seawater after chlorination (S2 location) had a little lower TOC and DOC ranges (2.2–7.2 & 0.9–3.2 mg/L) than the levels before chlorination (S1 location in Table IV) due to the oxidation effect of chlorine. However, the reported range of SUVA is very close to S1 range reflecting minimal effect of chlorination on the aromatic contents of NOM in the intake seawater. PAHs were also similar to those for S1 location where the samples of most sampled visits reported non-detected levels. The only exception was for few detected PAHs during September 2002 (0.12 ppb for Phenanthrene, 0.08 ppb for Anthracene, and o.32 ppb for Benzo[a] pyrene). In terms of THMs and HAAs, the table shows nominal levels of most components except bromoform (0.25–23.0 ppb) and dibromoacetic acid (0.52–13.4 ppb). It is clear that such bromo-halogenated organics did form after chlorination since they were originally at minimum levels before chlorination.

Samples were also collected twice for all locations (S2 to S20) for Phenols and PCBs analyses. Non detected levels for both groups were reported in those samples in the two sampling occasions.

The makeup seawater (S3 in unit 1 and S11 in unit 5) had a very close range of TOC, DOC, and SUVA to those of the intake seawater (S2) as they both originated from the same source. The main difference manifests in the higher formed halogenated organics, especially the bromoform levels that went up to 89 ppb in S3 and 41 ppb in S11, noting that less frequent analyses were done to unit 5, including S11. The high formed bromoform was related to the longer time duration for the seawater to travel from the intake point after chlorination to the distiller location.

It is apparent that the condensed bromoform into the distillate was ultimately accumulating to its maximum amounts after the final stage. Note that no detectable levels of any HAA5 component were reported in any of the collected samples in unit 1.

Analytical results of S18 and S19 in the final drinking storage tanks show that the formed bromoform was greatly amplified after post chlorination (27.6 ppb in S18 and 61.2 ppb in S19). To further evaluate the effect of reaction time on the formed bromoform, additional samples from the same locations were collected in January 2003 and left sealed in the ambient temperature for 48 hours after which they were preserved and analyzed. Higher levels were reported then, 38.7 ppb for S18 and 88.8 ppb for S19 with about 40–45% increase in formation. This significant increase draws the attention regarding the importance of tracking the formed bromoform in the water distribution system due to the travel time the water spends before it is finally consumed.

It is worth mentioning that the reported levels of bromoform approach the international limits set by various regulations. According to USEPA cancer risk classification, bromoform as well as chloroform are classified as B2 as it showed evidence of carcinogenicity. Stage 1 DBP Rule in 1998 promulgated a zero MCLG for chloroform, bromodichloromethane, and bromoform. Also, the MCLs were lowered by the same rule to 0.08 and 0.06 mg/L for TTHMs and HAA5, respectively. The *Stage 2 D/DBP Rule* lowered the MCLs for TTHMs and HAA5 to 0.04 and 0.03 mg/L, respectively, and was originally set to be enforced in May 2002. The available technology and related high costs represent the main arguments of groups opposing the enforcement of such limits. In Europe, the EC only provided a non-enforcing guiding limit of 1 μg/L for total haloforms and allowed the member states to adopt their own regulations. This encouraged some countries to establish their own standards, especially after the World Health Organization (WHO) published two editions of Guidelines for Drinking Water Quality (WHO, 1993) that included a comprehensive contaminant list including DBPs. England, for example, adopted a limit of 100 μg/L for TTHMs based on average of 3-month samples collected from designated water supply zone while in the Netherlands, a stringent limit of 5 μg/L for each THM individual species was adopted in 1993 (Evendijk, 1995) in addition to phasing out the chlorine as a disinfectant. A new EU directive on drinking water quality was drafted in 1998 and expected to come into force in December 2003. In United Arab Emirates, regulating the DBPs receives less attention from the water authorities.

Since TOC, DOC, and SUVA of S18 and S19 locations remain at reasonably low levels; the increased formation of bromoform appears to be brought about by chlorine addition to a distillate that still has a formation potential due to the presence of trace organic precursors. Blending the final distillate with a 0.2% chlorinated seawater in post-treatment processes may be also contributing to the increased formation of bromoform in these locations. The high levels of bromform in general and its proximity to the internationally regulated limits triggers the need of further investigation of the effect of blending seawater on such formation. This is achieved via laboratory-controlled experiments presented in the next section.

7. Artificial Chlorination of Distillate

The objective of this section is to evaluate the effect of seawater blending with drinking water upon the formation of THMs and bromoform. Such evaluation will help in identifying the source of organic precursors reacting with the chlorine added at post treatment stage to form the bromoform. These precursors may be either originated in the raw seawater and passes through the thermal desalination processes or increased due to the addition of the blending seawater.

Lab-controlled experiments were conducted using the distillate produced from the two considered units of Ruwais desalination plant (units 1 and 5). Two volumes of distillate were collected from the two units right before adding the chlorine, i.e.; upstream the distillate storage of Figure 1. The two volumes were brought to the laboratory and spiked with three different levels of chlorine (0.6, 1.2, and 2.4 mg/L) in well sealed 40 ml glass vials using high grade liquid sodium hypochlorite. Another patch of samples for each unit-distillate was prepared by blending a 0.2 volume percentage of seawater delivered from the intake location where the same three levels of chlorine were applied to the blended samples.

Since pH of the collected water were low; 7.1 for unit 1 and 7.4 for unit 5, another patch of samples was prepared from the distillate of unit 5 after raising its pH to 10.5 using the same phosphate salt applied in the site. Assessing the impact of seawater blending upon the bromoform formation for that patch was necessary to perceive the effect of increased pH on such impact given the fact that pH of the finished water (locations 18 and 19) is close 9.

THM analysis was carried out on each group of samples after 24 hours from the time of chlorine spiking. The samples were incubated during that period at a maintained temperature of 40 °C that simulates the site temperature. The results of these analyses are all plotted in Figure 2.

The results of this experiment show that bromoform, whose boiling point ranges from 146 to 150 °C, dominated the formed THM under all tested conditions in agreement with the past findings of field analyses. The level of formation increases with the chlorine level and with pH. The increase in TTHM was obviously dominated by bromoform increase. Comparing the results for the non-blended samples to the blended ones, it can be noticed that the blended samples experienced higher formation for bromoform and total TTHM than the non-blended samples. However, the increase in this formation was not significant and was always in the range of 5 to 20%. The maximum increases (up to 40%) were observed for the unit5-distillate with elevated pH when spiked with high chlorine levels (1.2 and 2.4 mg/L). Such conditions are rarely applied in the current ongoing practices so that the increased

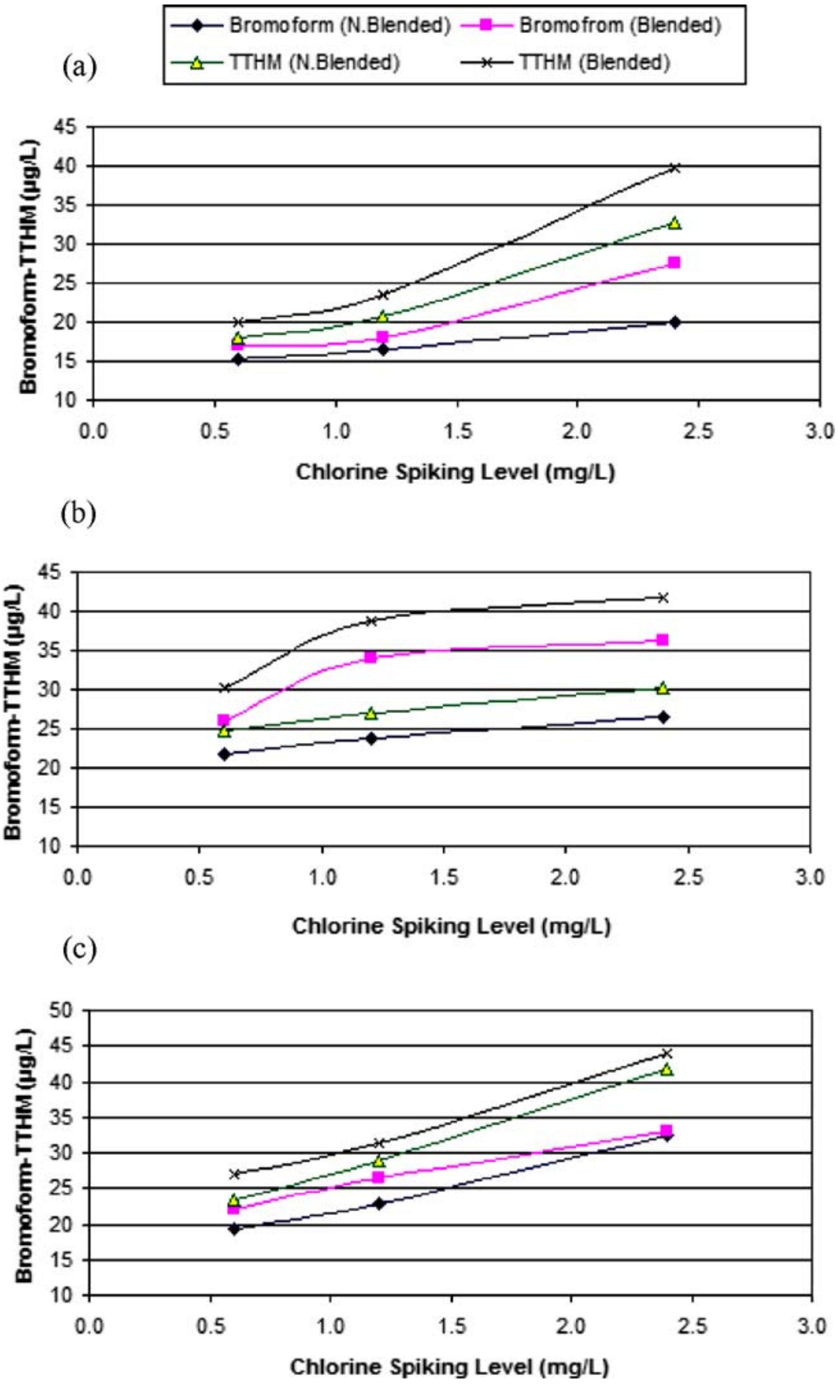


Figure 2. Bromoform and TTHM formation with chlorine spiking level for (a) Unit 1 – Distillate, (b) Unit 5 – Distillate, and (c) Unit 5 – Distillate with Elevated pH.

formation of bromoform due to blending the distillate with seawater is always less than 20% in most practical situations.

The above findings show that most of the formed bromoform in the final drinking water can be attributed to the following two possibilities:

(1) Bromoform already exists in the seawater intake and not removed by thermal desalination stages.
(2) New formed bromoform due to the reaction of chlorine added at post-treatment and the trace organic precursors not removed by thermal desalination.

8. Conclusion

Chlorination byproducts (CBPs) in drinking water produced from a thermal desalination plant in the United Arab Emirates has been investigated. Trihalomethanes and haloacetic acids were both tracked at the plant's influent and effluent and after several distillation stages inside the plant. Analysis of the tracked samples after various distillation stages indicated that the thermal processes do not totally remove the CBPs precursors originally found in the seawater. While trace levels of Haloacetic acids were reported in the effluent water, tangible levels of Bromoform were reported in the final distillate especially after post chlorination. Artificial spiking of the final distillate from two desalination units reflected insignificant contribution of the portion of seawater blended with the final distillate to the formed bromoform in the finished drinking water. The results show that most of the formed bromoform in the final drinking water can be attributed to either Bromoform that already exists in the intake seawater and not removed by thermal desalination stages, or the new formed bromoform due to the reaction of chlorine added at post-treatment and the trace organic precursors not removed by thermal desalination.

Quality of the intake water and its organic content was evaluated by analyzing three organic groups; Phenol, PAHs, and PCBs. Most individual compounds of all three groups were in the nearby of non-detected levels except for a number of PAH compounds that were reported high during the month of September 2002. The same three organic groups were tested inside the desalination plant after several distillation stages and were all found close to non detected levels.

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