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# Contamination of Residual Chlorine and Formation of Halogenated Hydrocarbons at the Vicinity of Desalination Plant in Kuwait

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**Abstract:** Seawater desalination is one of the major industrial activities along the coastline of Kuwait that poses profound environmental impact on the quality of seawater. This study focuses on investigating the potential contamination of biocides, volatile organic hydrocarbons (VOCs) and other halogenated hydrocarbons discharged from Az-Zour desalination plant. Chemical contamination by residual chlorine (RC) and some VOCs was detected in effluents from inside and at the vicinity of the plant. RC ranged between 0.15 and 0.49 mg/L while bromoform ($CHBr_3$) was the highest of all the VOCs detected and ranged between 0.22 and 3.30 μg/L. Benzinoides (benzene, toluene, xylene and ethylbenzene) were also detected at 0.1 μg/L and 0.25 μg/L. The levels of RC as measured in the vicinity of the Az-Zour plant are below the limit set up by Kuwait EPA. However, it still poses effects to the nearby aquatic life and therefore, it is important to lower the concentration of RC in the discharge effluent.

**Key words**: Desalination, impact, seawater, biocides, assessment.

## 1. Introduction

In Kuwait, water resources are very limited and most of the fresh water is produced by desalting Gulf seawater. During the last five decades, Kuwait has developed six multi stage flash (MSF) dual-purpose plants for water production and power generation, along a 120-km shoreline [1]. Seawater desalination by MSF process generally requires a large seawater inlet flow resulting in an increase in salinity of the discharge flow known as brine. Various chemicals are added to the feed water to control formation of mineral scale and biological growth that would otherwise interfere with the processes [2-4]. These chemicals or their reaction products are in turn discharged with the reject brine. The introduction of concentrated brine waste effluent has been historically considered a major environmental concern with desalination plants particularly on marine ecosystem. The discharged brine is characterized by increased salinity and elevated temperature. It additionally contains substantial amounts of chemical pollutants, such as chlorine, antiscalants and heavy metals. Chemical contamination by residual chlorine (RC) and some volatile organic hydrocarbons (VOCs) was detected in effluents from inside and at the vicinity of the desalination plants [5-8]. The purpose of this paper is to study the possible formation of trihalomethanes (THMs) in seawater and to quantitatively change concentrations of biocides and impacts caused by the effluent discharged from Az-Zour desalination plant in Kuwait on the local marine environment.

### *1.1 Environmental Effects of Chlorine Gas*

Chlorine is added directly to the seawater to control biofouling and usually present in the brine of the MSF plant. The added chlorine reacts with bromide and

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other compounds in the water to produce a wide range of chemical oxidants. Chlorine transforms bromides to bromine, while the chlorine itself is transformed to chloride. These brominated products are the active forms of biocide in seawater systems and their relative concentrations change on time scales from fractions of seconds to days [9]. Additionally, the brominated residual biocide can react with natural organic matter in the seawater to form a number of halogenated organic compounds that are toxic to aquatic life as well as humans. Several studies have investigated chlorine concentrations adjacent to desalination plant outfalls. Ali and Riley [10] reported levels of 30-100 μg/L and Abdel-Jawad and Al-Tabtabaei [3] estimated a level of 50 μg/L at a 1-km distance from the outlet, both referring to the coastal waters of Kuwait. Some authors concluded that the impact of RC with low concentration on the marine environment is insignificant and becomes undetectable at a distance less than one kilometer from the discharge location along the coastline [3, 11, 12]. On the other hand, chlorine is highly toxic even at low levels, and this conclusion can be verified by several toxicological results [13].

### *1.2 Environmental Effects of Halogenated Hydrocarbons*

Halogenated hydrocarbons are by-products resulting from chlorination process of contaminated seawater in the MSF desalination plants. Halogenated hydrocarbons arise either from reaction with precursors of natural origin, which will predominantly produce THMs or with petroleum components, for example, giving rise to chlorophenols or chlorobenzenes [14]. However, the number of by-products can hardly be determined due to many possible reactions of hypochlorite and bromite with organic seawater constituents, and the already complex chemistry of chlorine in seawater is deteriorated by high oil pollution in the Arabian Gulf [15]. Few studies were conducted to determine the levels of THM close to outfall of desalination plants in Kuwait. A study conducted in 1986 reported high THM levels (up to 83 μg/L) in the outfall site of Shuwaikh in Kuwait Bay, which decreased to less than 1 μg/L within 2- to 4-km distance [10]. Other authors investigated the levels of halogenated hydrocarbons in coastal waters of Kuwait, and their results indicated that the levels and composition depend on desalination plants location [14]. The THM levels according to this study varied between 0.001 and 2.7 μg/L in Kuwait Bay and were considerably higher close to the outlet, ranging between 0.1 and 9.5 μg/L.

## 2. Material and Methods

### *2.1 Study Area and Sampling Locations*

Az-Zour power-desalination plant is one of the six sites that produce distilled water in Kuwait using MSF technology. The plant is located 120 km south of Kuwait and designed to produce 0.65 million $m^3$/d. In this study, a total area of about 2 km at the vicinity of the marine area of the plant was assessed as shown in Fig. 1. Transects were established perpendicular to the coast and extend 2 km north and south or east and west from the outfall channel, taking into consideration the local condition and the technical specification of the intake and outfall channel. About 15 to 20 sampling points from 3 to 5 transects were selected, and sampling stations at successive increasing intervals from the outfall point were identified by global positioning system (GPS). Two water depths including surface and bottom were included in the assessment at these sites when feasible.

### *2.2 Sampling Procedure*

Two sampling programs were carried out in the study. The first field sampling program was carried out between 6 and 28 August 2007. This program represented the summer season. The second sampling was carried out between 18 February and 25 March 2008

**Fig. 1 Az-Zour desalination plant and outfall structure.**

and represented the spring season. The sampling programs were hampered by the prevailing weather conditions, and thus, were done when conditions allowed. The surveyed stations with their GPS locations and water depth are shown and given in Table 1 and Fig. 2. Sampling was conducted according to the Regional Organization for the Protection of Marine Environment (ROPME) Manual [16].

*2.3 Measurements and Analytical Methods*

The laboratory chemical analyses of collected seawater included measurement of petroleum-related hydrocarbon (total petroleum hydrocarbons (TPHs)) and total organic carbon (TOC) content. Water samples were also collected from beneath the seawater surface and transferred to a prechilled 40-mL amber vials specially purchased for VOC sampling and analyses as shown in Fig. 3. The work of all chemical analysis to determine the elements chemical readings was made according to the standard methods [17]. Measurements of RC were done in the field using Palintest 1000 Chlorometer-DUO (Palintest, England) with DPD chlorine tablet photometer grade in the range of 0-5.00 mg/L. The Palintest DPD-free tests are approved by the US-EPA as accepted versions of the Standard Method 4500-C1-G. Determination of VOCs in the water samples was made according to EPA method 524.2 (Eichelberger and Buddle, 1989) and performed by central analytical laboratory (CAL). Sixty VOCs listed in this method were analyzed including the THMs.

## 3. Results and Discussion

*3.1 RC*

Chlorination by addition of chlorine gas is used as antifouling agent in intake water of the desalination plants in Kuwait. Low concentrations (2-4 mg/L) are added continuously, although higher concentrations (8 mg/L) are injected intermittently every 8 h for 20 min. Remaining chlorine residue referred to as free chlorine (or RC) is discharged with the effluents through the plant outlets to the nearby marine environment. RC was measured in both surface and bottom water layer at the vicinity of the plant according to the sampling sites shown earlier (Fig. 2). RC was detected at all the stations in different concentrations that ranged between

**Table 1 Location and water depth of sampling stations at the study area of Az-Zour Desalination Plant.**

| Station code | Distance (m)** /transict | GPS coordinate North | GPS coordinate East | Water depth (m)* |
|---|---|---|---|---|
| Zr 1 | 100 E | 28.69843 | 48.37995 | 1.7 |
| Zr 2 | 300 SE | 28.69688 | 48.38183 | 5.2 |
| Zr 3 | 100 S | 28.69774 | 48.37962 | 2.5 |
| Zr 4 | 100 N | 28.69981 | 48.38006 | 4.8 |
| Zr 7 | 300 NE | 28.7 | 48.38006 | 5.4 |
| Zr 8 | 500 SSE | 28.69366 | 48.38226 | 4.6 |
| Zr 9 | 500 ESE | 28.69398 | 48.38793 | 5.5 |
| Zr 10 | 800 NE | 28.70015 | 48.3866 | 5.4 |
| Zr 11 | 500 NE | 28.70155 | 48.38408 | 5.3 |
| Zr 12 | 1000 ESE | 28.69398 | 48.38793 | 5.8 |
| Zr 13 | 1000 E | 28.6979 | 48.3899 | 6.1 |
| Zr 14 | 1000 SE | 28.691 | 48.3878 | 5.6 |
| Zr 15 | 1000 NE | 28.70298 | 48.38868 | 8.9 |
| Zr 16 | 2000 SE | 28.6892 | 48.39591 | 5.0 |
| Zr 17 | 2000 E | 28.6971 | 48.39883 | 6.6 |
| Zr 18 | 2000 SSE | 28.68405 | 48.39 | 4.0 |
| Zr 19 | 2000 ESE | 28.69037 | 48.39693 | 6.7 |
| Zr 20 | 600 N | 28.70376 | 48.38723 | 3.3 |
| Zr 21- Control | 2000 NE | 28.70758 | 48.39723 | 7.0 |

* Depth as measured at the time of sampling.

** Distance and direction from the outfall point; N (North); NE (Northeast); E (East); S (South); SE (Southeast); SSE (Southsoutheast); ESE (Eastsoutheast).

0.06 and 0.25 mg/L in surface water with an average 0.13 ± 0.01 and between 0.01 and 0.25 mg/L in bottom water with an average 0.13 ± 0.02 as demonstrated in Table 2.

In addition, RC was also monitored in the brine discharged from the distillation units at the plant site before mixing with the cooling water (i.e. effluent discharged to the syphon shaft) and at the mixing zone (distillation effluent and power cooling effluent mixture) and found to be 0.18 and 0.1 mg/L at these two points, respectively.

According to Kuwait EPA guideline for industrial wastewater, the level of RC should not exceed 0.5 mg/L in the effluent discharged to the sea. Results obtained in this study comply with these standards. The importance of lowering the limit of RC in the discharge of desalination plants derived from the claim that even at low mg/L levels, RC can have toxic impacts on the marine organisms in the near shore environments as indicated by several studies [18-20]. Although levels of RC as measured in the vicinity of the Az-Zour plant are below the limit set up by Kuwait EPA (< 0.5 mg/L), it still poses effects to the nearby aquatic life as shown by these studies. Hence, further control measures are required by the regulating authority in Kuwait supported by further studies to verify these impacts.

### *3.2 Formation of Halogenated Organics*

As chlorine is added to intake water to reduce biofouling, the remaining RC discharged to the sea can react with organic compounds both naturally occurring in seawater and organic contaminants such as hydrocarbons present in the vicinity of the outfall. This reaction will lead to the formation of anthropogenic halogenated hydrocarbon, so-called disinfection by-products that are known for their carcinogenic properties. The most commonly detected of these compounds are the THMs, although other volatile organic compounds are also associated with

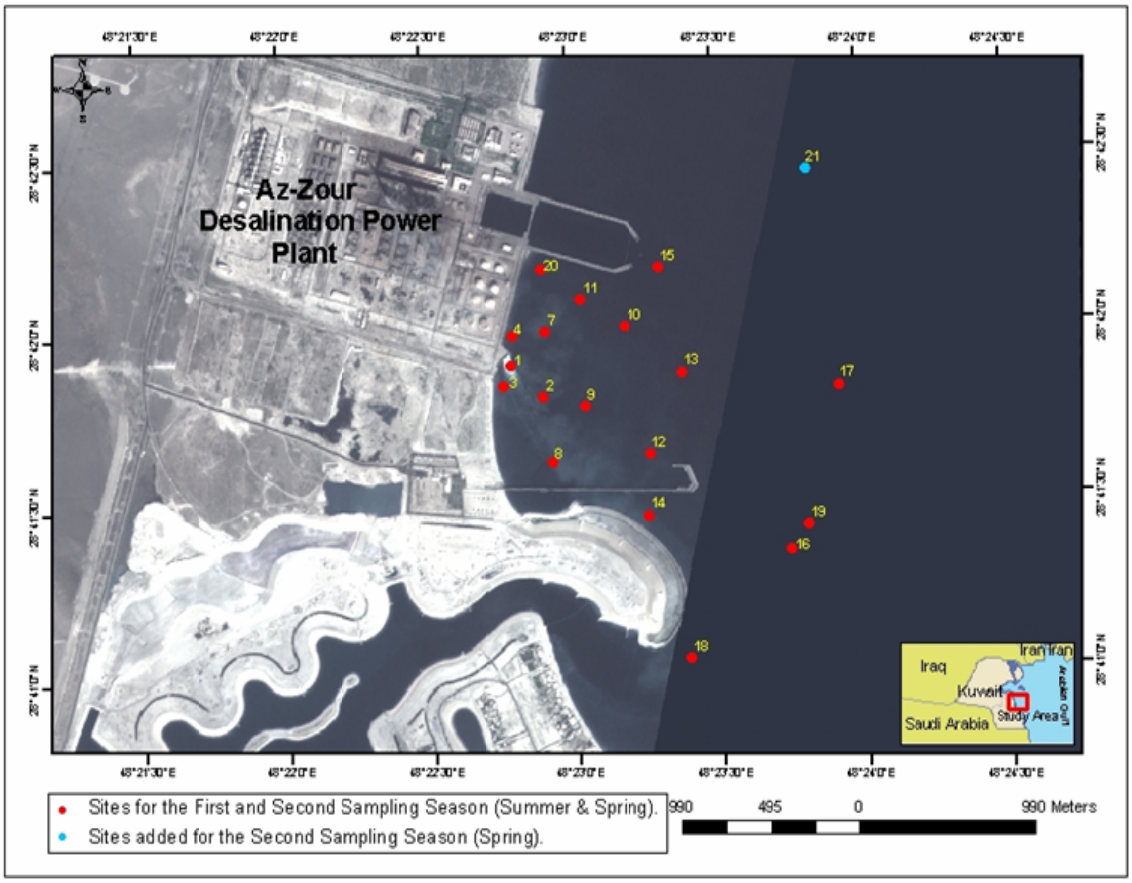


**Fig. 2** The sampling stations at the study area of Az-Zour desalination plant.

**Fig. 3** Collection of water samples for VOC analysis.

**Table 2 RC measured at the vicinity of Az-Zour Desalination Plant.**

| Station code | Seawater level | RC (mg/L) |
|---|---|---|
| Zr-1 | Top. | 0.12 |
| | Bott. | 0.13 |
| Zr-2 | Top. | 0.06 |
| | Bott. | 0.05 |
| Zr-3 | Top. | 0.19 |
| | Bott. | 0.23 |
| Zr-4 | Top. | 0.14 |
| | Bott. | 0.09 |
| Zr-7 | Top. | 0.08 |
| | Bott. | 0.09 |
| Zr-8 | Top. | 0.16 |
| | Bott. | 0.14 |
| Zr-9 | Top. | 0.25 |
| | Bott. | 0.05 |
| Zr-10 | Top. | 0.13 |
| | Bott. | 0.25 |
| Zr-11 | Top. | 0.13 |
| | Bott. | 0.15 |
| Zr-12 | Top. | 0.15 |
| | Bott. | 0.17 |
| Zr-13 | Top. | 0.15 |
| | Bott. | 0.15 |
| Zr-14 | Top. | 0.24 |
| | Bott. | 0.18 |
| Zr-15 | Top. | 0.09 |
| | Bott. | 0.13 |
| Zr-16 | Top. | 0.12 |
| | Bott. | 0.01 |
| Zr-17 | Top. | 0.11 |
| | Bott. | 0.11 |
| Zr-18 | Top. | 0.13 |
| | Bott. | 0.14 |
| Zr-19 | Top. | 0.08 |
| | Bott. | 0.23 |
| Zr-20 | Top. | 0.06 |
| | Bott. | 0.06 |
| Zr-21 (Control) | Top. | 0.13 |
| | Bott. | 0.18 |
| Max | Top. | 0.25 |
| | Bott. | 0.25 |
| Min | Top. | 0.06 |
| | Bott. | 0.01 |
| STDEV | Top. | 0.052 |
| | Bott. | 0.066 |
| Avrg ± STD error | Top. | 0.13 ± 0.01 |
| | Bott. | 0.13 ± 0.02 |

desalination and power plant activities. According to USEPA, THMs constitute the sum of the concentrations of four compounds: chloroform ($CHCl_3$), bromoform ($CHBr_3$), diobromochloromethane ($CHBr_2Cl$), dichlorobromomethane ($CHCl_2Br$). The level of THMs is influenced by RC concentration, temperature and TOC and pH levels [21]. At the vicinity of the marine area of the plant, VOCs including toluene, ethylbenzne, xylene and tribromomethan were detected in water in relatively low concentrations as shown in Table 3. Toluene ranged between 0.1 μg/L and 0.22 μg/L. Ethylbenzene was 0.11 μg/L while xylene was between 0.13 and 0.25 μg/L. The source of these compounds is oil contamination. These results are in agreement with the findings of a previous study on the vicinity of Az-Zour desalination plant. In that study, the presence of these compounds was attributed to the petroleum activities in the north of the plant [14]. As shown in Fig. 4 the concentration of $CHBr_3$ was the highest of all the VOCs detected and ranged between 0.22 and 3.30 μg/L. The highest concentration was detected at station Zr 18 (2000 m SSE) which is located at the entrance of Khor Al-Mefateh southward of the discharge outlet.

In water collected from inside the plants, $CHBr_3$ was detected in the reject brine of the distillation units (before mixing with the cooling water) and in the effluent released from the PP at concentration of 11.2 μg/L and 10.1 μg/L, respectively (Table 4). However, the concentration was reduced to 7.5 μg/L at the mixing zone of the outfall showing a 1.5-fold reduction

**Table 3 Concentration of volatile organic compounds (μg/L) (measured in water at the vicinity of Az-Zour Desalination Plant).**

| Station | Toluene | Ethyl benzene | Xylene | Tribromomethane $CHBr_3$ |
|---|---|---|---|---|
| Zr 1 | n.d. | n.d. | n.d. | 0.22 |
| Zr 8 | 0.22 | 0.11 | 0.13 | 2.41 |
| Zr 9 | 0.21 | 0.11 | 0.13 | 2.54 |
| Zr 18 | 0.10 | n.d | 0.25 | 3.30 |

All samples were spiked with 50 μL of 10 mg/L of EPA 524.2 fortification solution containing fluorobenzene, 1,2-dichlorobenzene-D4 and 4-Bromofluorobenzene to give a final concentration of 12.5 mg/L in each 40 mL sample.
Recovery range was: 86-100%. The detection limit range is 0.019-1.6 μg/L.
n.d.: not detected.
Distance/direction from outfall: Zr 1 (100E), Zr 8 (500 SSE), Zr 9 (500 ESE), Zr 18 (2000 SSE).

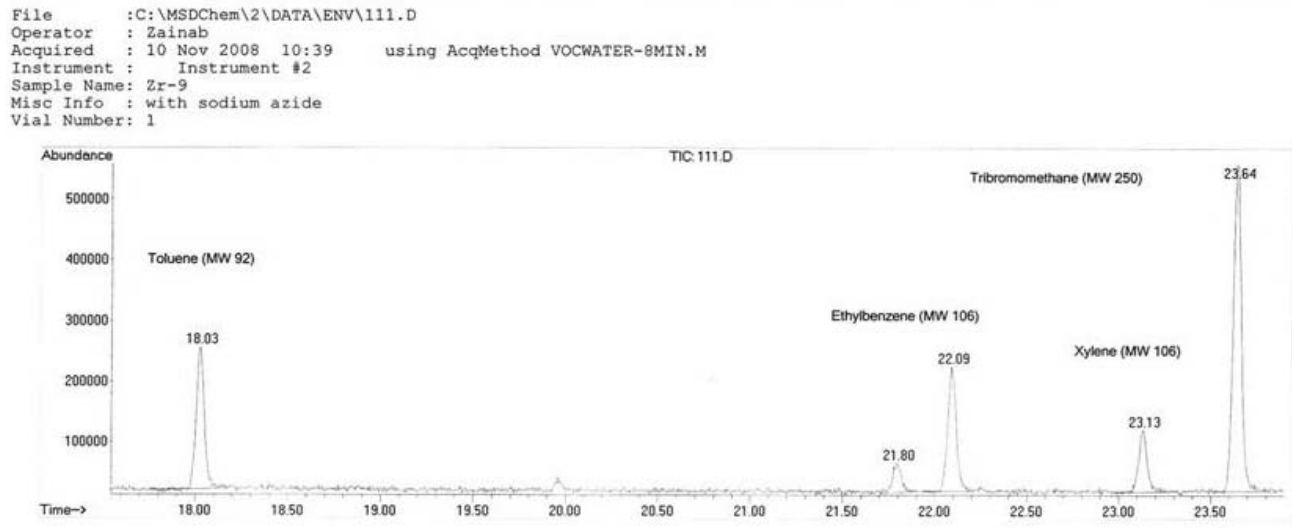


**Fig. 4 VOCs detected at the vicinity of Az-Zour desalination and power plant.**

**Table 4 Concentration of VOCs (μg/L) (measured in effluents from Az-Zour Desalination Plant).**

| Sample code | Toluene | Ethyl benzene | Xylene | $CHBr_3$ |
|---|---|---|---|---|
| Brine from distillation units | n.d. | n.d. | n.d. | 11.2 |
| Power plant effluent | n.d. | n.d. | n.d. | 10.1 |
| Outfall (mixing zone) | n.d. | n.d. | n.d. | 7.5 |

Recovery range was: 86-100%. The detection limit range is 0.019-1.6 μg/L. n.d.: not detected.

from original concentration in the brine released from the distillation units. No other VOCs were detected in these waters. It has to be mentioned here, concentration of chlorine was measured at these locations and found to be 0.18 and 0.1 mg/L, in the effluent released from the distillation and power units, respectively.

Several authors investigated the occurrence of the halogenated volatile compounds associated with desalination and power plant effluent discharge. They found several halogenated volatile liquid hydrocarbons (HVLHs) in the coastal areas adjacent to Az-Zour desalination plant. Benzinoides (benzene, toluene, xylene and ethylbenzene) were also detected at a range from 187 to 12,471 ng/L at Az-Zour desalination plant. The presence of the compounds was related to oil contamination [14]. Other study, four THMs were consistently detected in the brine waters with bromoform ($CHBr_3$) accounting for 90% of the total THMs followed by $CHBr_2Cl$. According to the findings of these authors, THMs ranged from 90 ng/L in the immediate vicinity of the discharge point to less than 1 ng/L within few kilometers seawards [10]. Environmental concerns over THMs in the marine environment stem from not only the direct impact of these compounds on the aquatic ecosystem surrounding the desalination and power plants, but also on the possibility of contamination of the potable water condensate by these low boiling point compounds that can reach the desalination plant intakes and re-circulate within the system. Guidelines for levels of THMs in water vary from a country to a country. The Gulf Cooperation Council has set maximum permissible level of 200 μg/L for THMs [21].

## 4. Conclusion

The levels of RC as measured in and at the vicinity of the Az-Zour desalination plant are below the limit set up by Kuwait EPA regulations (< 0.5 mg/L). However, the total amount discharged is large because of the high volume of seawater used for plant operations. At the vicinity of Az-Zour plant, both $CHBr_3$ and benzinoides (benzene, toluene, xylene and ethylbenzene) were detected. Concentration of $CHBr_3$ was the highest of all the VOCs detected. In order to further lower the permissible levels of THMs associated with desalination effluent discharge, it is important to lower the concentration of RC in the discharge for its major role in the formation of these contaminants. Hence, further control measures are required by the regulating authority in Kuwait supported by further studies to verify the impacts. In addition, it is important to determine the minimum amounts of chlorine that are effective in preventing biofouling in desalination plants in Kuwait.

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