

**Sources and levels of trihalomethanes in Suez bay water:
Attaka power station (case study)**

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ABSTRACT

Trihalomethanes have been identified as one of the most important disinfection byproducts resulted from using hypochlorite in power stations. So, Attaka power station was chosen as a case study which used hypochlorite as biological fouling control in its cooling seawater system. Water samples were collected monthly during 2016-2017 from four sites in the inlet, outlet, after dosing hypochlorite and at mixing point. The seawater samples were analyzed for water temperature, pH value, salinity, oxidizable organic matter, total residual chlorine and trihalomethanes (THM's). The results showed that the two main forms of THMs formed in the receiving seawater were bromoform and dibromochloromethane. The bromoform compound was fluctuated between 12.16ppm and 237.25ppm with a mean value of 77.23 ppm and with a total annual of 926.76ppm, while dibromochloromethane ranged from 0.28 to 4.20ppm. Significant positive correlation was found between trihalomethanes fractions and both of the measured concentrations of the total residual chlorine and organic matter, while negative correlations with water temperatures and pH values were noticed. No correlation between trihalomethanes and salinity was recorded.

Key words: Trihalomethanes, residual chlorine, Attaka power station, disinfection byproducts.

INTRODUCTION

The power stations, desalination plants and oil refineries which built on the sea shore coast and depend on seawater in their cooling systems suffer from the growth and reproduction of marine fouling organisms in tunnels and pipelines of their cooling system causing blocking and clogging the entrance of seawater, which leads to the inefficiency of the station of electricity and often come out of operation (Fisher *et al.*, 1991; Videla, 1995). Power stations and desalination stations use several methods to resist marine fouling organisms, for example adding hypochlorite to seawater at the entrance of the power plant (Sakaguchi *et al.*, 1989; Katranitsas *et al.*, 2003). One of the harmful effects on marine environment is the chemical reaction between the total residual chlorine come out from these power plants and the organic matter in seawater, forming Trihalomethanes (Kampioti and Stephanou, 2002). The presence of bromine in seawater leads to the formation of bromoform, which has a significant effect on the growth of some marine fouling organism (Saeed *et al.*, 1999). Bromoform is formed by the oxidation of bromide by chlorination, leading to the formation of bromine compounds. THMs in chlorinated seawater mainly consist of bromoform CHBr_3 (Sakaguchi *et al.*, 1989), dibromochloromethane CHBr_2Cl , dichlorobromomethane CHBrCl_2 , chloroform CHCl_3 (Sakaguchi *et al.*, 1989). Bromoform has a slow and progressive formation, being the final product in the oxidation of organic substances, and by research in the scientific references we did not find any reference or data

published about this point in the area under investigation, but there are many studies and researches in other parts of the world (Parsons *et al.*, 1984; Sugita *et al.*, 1992).

MATERIALS AND METHODS

Study Area and sampling

Attaka power station located on the Suez bay coast (Suez Gulf), Egypt. Seawater was drawn from the sea to the power station at Attaka through tunnel and it was used for cooling the main condensers and auxiliary systems like the process seawater heat exchangers. Seawater was drawn (about 26 m³/sec pumping seawater to the power station by 8 pumps) through a 500m long submarine intake tunnel. The intake water was doused by hypochlorite solution to inhibit the biomass of fouling organisms. The outcome water from the condenser and processes seawater heat exchangers was discharged into the Suez bay seawater and mixed with the coastal water which characterized by strong tidal currents.

Surface seawater samples were collected monthly using Nansen bottle from four sites, inlet point site I (seawater of Suez bay), after dosing hypochlorite site II (seawater after injection of hypochlorite solution)), outfall point III (seawater loaded by residual chlorine and thermal pollution) and mixing point site IV (effluents after mixed with seawater) during the period November 2016-September 2017 (Fig. 1). The sampling point at the inlet point was located far from the intake water to devoid any chlorine and notionally representative of the ambient water body.

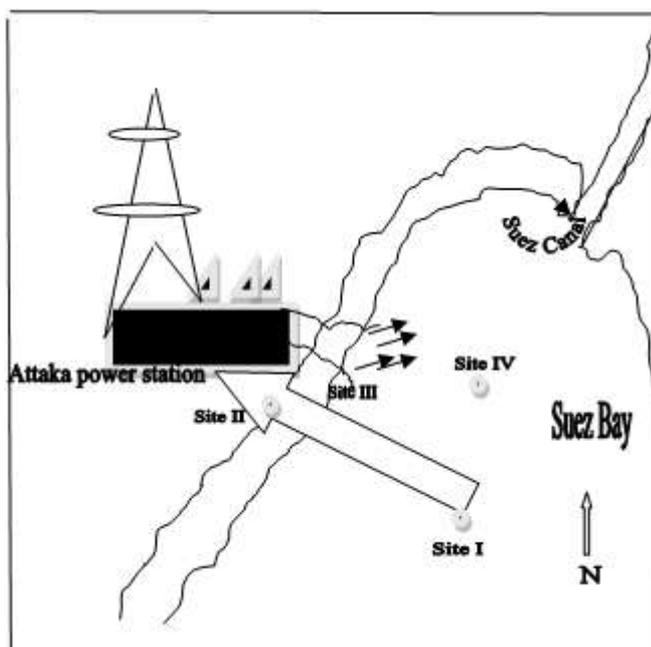


Fig.(1)Sampling stations in front of Attaka power station on the Suez bay coastal (not scaling).

Determination of total residual chlorine and seawater characterization

Free, combined and total chlorine concentrations were determined by colorimetric DPD method using a Thermo scientific Orion TM AQ3070 AQUA fast TM Chlorine Meter.

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DPD free Chlorine package was added to 10 ml of water sample where free available chlorine (Hypochlorous acid and the hypochlorite ion) in the sample oxidizes DPD causing a magenta red color. (Total Residual Chlorine =Free Residual Chlorine +Combined Residual Chlorine).

Determination of THMs

THMs were quantified by liquid/liquid extraction with n-pentane with ratio (5 ml sample: 1 ml n-pentane), and then shaking for 5 min. Then 3L of the extract was injected in gas chromatograph model Hewellett-Packard HP-5890 series II with Electron Capture Detector (ECD) according to Standard Method 6232 (APHA, 2005). Capillary column HP-1 with specifications, 30 m- 0.53 mm ID and 0.5 mm film thicknesses was used in this study. Carrier and make-up gas was pure nitrogen (99.999% purity).

RESULTS AND DISCUSSION

Five electric power stations were constructed on the northern part of the Gulf of Suez at the entrance of the Suez Canal. All the power stations depend on seawater in the their cooling systems. One of these stations, is Attaka power station which was chosen to study its outfall water loading by total residual chlorine and its role in the formations of trihalomethanes. All these stations use the hypochlorite for the control of marine fouling organisms.

Attaka power station suffers from the fast and heavy growth of fouling organisms in its cooling system and tunnel which draw the seawater from the Suez Gulf to the entrance of the station. The fouling organisms causing the drop of efficiency of cooling system of this station and sometimes some of its units get out of work due the block of many of heat exchangers tubes by fouling organisms (about 40-65 tons of sessile marine organisms had to be removed from the pipeline during a single cleaning, personal communication). Monthly fouling biomass accumulated on PVC panels and wood panels at the entrance of Attaka power station has been studied by Soliman and Yassin (2007) and the results are summarized Table (1) and Figure (2).

Table (1). Monthly fouling biomass wet weight g/panel accumulated on PVC and wood panel at the inlet of seawater at the entrance of Attaka power station during 2006.

Month	Jan-2006	Feb-2006	Mar-2006	Apr-2006	May-2006	Jun-2006	Jul-2006	Aug-2006	Sep-2006	Oct-2006	Nov-2006	Dec-2006
PVC	19.0	185.0	82.0	167.0	29.0	217.5	84.5	372.5	112.5	699.5	202.5	1009.5
Wood	38.0	60.0	73.0	25.0	45.5	94.0	96.0	24.0	217.5	58.5	417.5	520.0



Fig. (2). Fouling organisms accumulated on PVC (1) and wood panel at the inlet of seawater at the entrance of Attaka power station during 2006.

Hypocrite was used to control the marine fouling organisms. The hypochlorite in Attatka power station was produced using dissociation of sodium choired which exist in seawater by electric cells containing platinum electrodes and the produced hypochlorite was injected in the cooling seawater at the inlet of power station on the sea. Active chlorine solutions, whether created hypochlorite's, or comprise one or more of three different species—molecular chlorine (Cl_2).

Some of the remaining chorine residual escape to the marine environment, where the residual chorine react with organic matter (the main source of organic matter coming from the wastewater treatment plant which pumping the treated wastewater to the sea thorough a tube far away from the beach by about 500m) forming the THMs (bromoform CHBr_3 , dibromochoromethan CHBr_2Cl , dichorobromomethan CHBrCl_2 , choroform CHCl_3 (Krasner *et al.*, 1989) (Fig. 3).

Unfortunately, there were no studies before on the levels and sources of THMs in Suez bay as a result of using hypochlorite in the cooling systems in spite the presence of five power stations in the northern part of Suez Gulf which uses the same technology in control the fouling organism and this is the first case study which investigated this point. There are many studies in other areas addressed the significant effect of the organic matter on the chlorine residual as a source of halogenated organic compounds (Wong *et al.*, 1977; Allonier *et al.*, 1999).

Trihalomethanes (THMs) is produced by the reaction of the residual chlorine with organic matter in seawater (Nebo *et al.*, 2006). The levels of trihalomethanes (THMs) depends on several factors, such as the water temperature, pH value, total residual chlorine....etc (Goodman, 1987; Iriarte *et al.*, 2003; Acero *et al.*, 2005; Rodriguez *et al.*, 2007).

At Attaka power station, the characterization of seawater collected from the location near the inlet of cooling seawater indicated that the temperature values ranged between 18

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and 27°C, pH between 8.0 and 8.2, salinity between 41.5 and 42.98‰ and the particulate organic matter between 0.19 and 0.88 mg/l (Table 2).

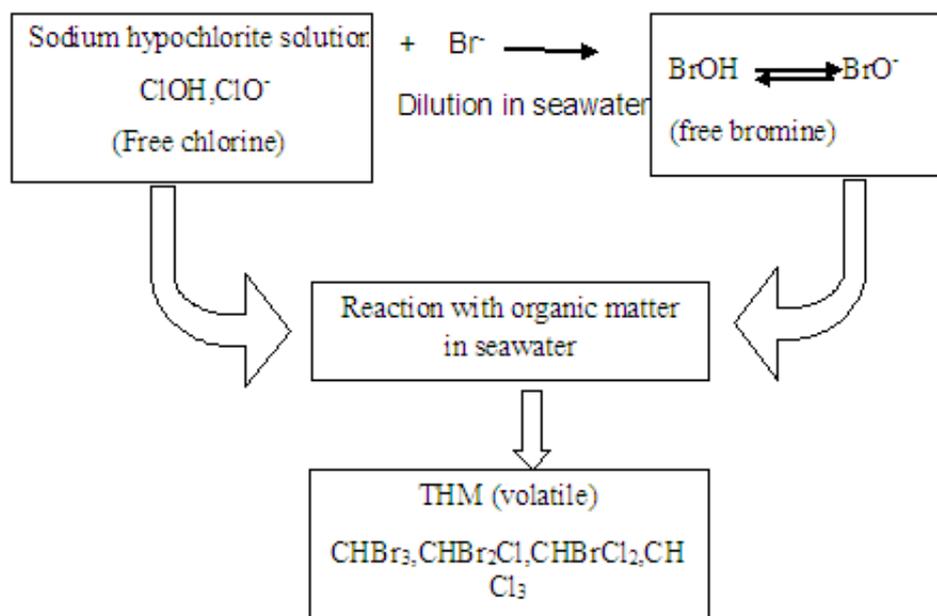


Fig. (3). The chemistry consequent upon sodium hypochlorite injection in natural seawater

Table (2). Seawater temperature (°C), pH-value, salinity‰ and dissolved organic matter mg/l of seawater in front of Attaka power station during 2016-2017

Parameter Date	Nov-016	Dec-016	Jan-017	Feb-017	Mar-017	Apr-017	May-017	Jun-017	Jul-017	Aug-017	Sep-017	Oct-017
T C°	19.58	18.94	18.3	17.5	18	21.25	24.03	26.8	26.91	27.01	23.3	22.12
pH	8.3	8.38	8.45	8.25	8.35	8.36	8.3	8.39	8.46	8.39	8.22	8.12
Salinity ‰	42.35	42.98	41.53	41.53	41.75	41.97	41.06	40.15	41.66	42.41	41.16	423
DOM mg/l	1.55	1.27	1.29	0.88	0.76	0.65	0.28	0.91	0.96	0.99	1.00	0.88

Temperature plays a vital role in speeding the kinetics reaction between chlorine residual and organic matter (Acero *et al.*, 2015). There was a negative correlations between seawater temperatures and levels of total chlorine residual at site II and site III, dibromochloromethan CHBr_2Cl (Site II), bromoform CHBr_3 (Site II), dibromochloromethan CHBr_2Cl (Site III) and bromoform CHBr_3 (Site IV). This may reflect the effect of temperature on the rate of evaporation of THMs which distinguished by low boiling point and low solubility in water (Table 3).

There was also a negative inverse relationship between pH values and THMs compounds. An increase in pH results in a decrease in residual chlorine concentration and

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consequently a decrease in the concentration of THMs compounds (Table 3). Nearly no correlation was found between salinity and trihalomethanes compounds. As for the effect of organic matter, it was found that there was a good relationship with most of THMs compounds.

Table (3). Relationship between total chlorine residual (mg/l), temperature (°C), pH, salinity (‰), particulate organic carbon (mg/l) of seawater and bromoform (µg/l)

	CHBr ₂ Cl Site II	CHBr ₃ Site II	CHBr ₂ Cl Site III	CHBr ₃ Site III	CHBr ₃ Site IV	residual chlorine Site II	residual chlorine Site III	T C°	pH	Sal ‰	DOM mg/l
CHBr ₂ ClSite II	1.00										
CHBr ₃ Site II	.19	1.00									
CHBr ₂ ClSite III	1.00	.19	1.00								
CHBr ₃ Site III	-.41	.57	-.41	1.00							
CHBr ₃ Site IV	.52	.52	.52	.26	1.00						
residual chlorine Site II	.45	.85	.45	.29	.72	1.00					
residual chlorine Site III	.42	.73	.42	.19	.71	.91	1.00				
T C°	-.45	-.01	-.45	.32	-.56	-.20	-.32	1.0			
pH	-.47	-.15	-.47	.20	-.12	-.30	-.21	.19	1.0		
Salinity ‰	-.11	.01	-.11	-.17	-.34	-.08	-.07	.01	-.67	1.0	
DOM mg/l	.09	.71	.09	.40	.60	.54	.56	-.28	.18	-.07	1.00

The levels of total residual chlorine and trihalomethanes (THMs) in Suez bay water at the investigated four sampling sites are given in Tables (4 &5). It was obvious from Table (3), that the values of the total residual chlorine at sites I (Inlet seawater) and Site IV (Mixings point) lie under detection limit (<0.1). At site II the total residual chlorine ranged between a minimum of 0.51ppm in November 2016 to a maximum of 0.11ppm in Feb, 2016, June 2017 and July 2017 with a mean value of 0.22ppm and with annual discharge about 2.71ppm, while at site III the residual chlorine lies in the range 0.05-0.22ppm, the minimum values were recorded in February-2017 and August-2017 while the maximum one was noticed in Sep-017 with a mean value of 0.10ppm and total discharges about 1.24ppm.

It was clear from Table (4) that trihalomethanes at site I, are nearly not detected in most months and reached about 1.10 ppm and 0.90 ppm at Aug-017 for dichlorobromomethane and bromoform, respectively. At site II, bromoform fluctuated between 12.16ppm at Feb-016 and 237.25ppm at Nov-017 with a mean value of 77.23 ppm and total annual of 926.76 ppm, Dibromochloromethane than were found in levels of 4.20, 3.11, 3.02, 4.01, 2.14, 0.28, 3.12 and 1.12 ppm, respectively while chloroform and dichlorobromoform are not found in all months of study. At Site III, only dibromochloromethane and bromoform are found and ranked between a minimum of 2.14 ppm for and

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13.46ppm for dibromochloroform than and bromoform, respectively at Jun-017 and Apr-017 while a maximum values of 5.00 and 62.13ppm are found at Feb-017 and Aug-017 with a mean values reached about 3.31 and 42.36 ppm. At site IV, the dibromochloroform than ranged from not detected to the maximum value (about 4.09 at Sept. 2017), while the total bromoform which enters the marine environment was about 232.13ppm during 2016-2017. The minimum value of 4.61ppm was observed at Oct-017, while the maximum value (40.00 ppm) was noticed at Sept. 2017.

Table (5) indicated that the values of bromoform and dibromochloroform than were nearly detected at all sites. Chloroform is the major THMs formed at power stations used freshwater as source of cooling water, whereas bromoform is predominate at power stations used seawater as source of cooling water in estuarine and marine sites. On the other hand, seawater contains approximately 68 mg/l bromide at full salinity, when chlorine is added it oxidizes the bromide ions yielding hypobromous acid HOBr. This reaction is rapid, with 99% conversion with 10s at full seawater salinity and within 15s even at half seawater salinity (full salinity of Suez bay water ranged between 41.5 and 42.98‰). The free oxidants formed by the chlorination of seawater are thus predominantly composed of HOBr and the hypobromite ion OBr⁻. At the ambient pH of seawater this free oxidant is essentially dissociated and consequently more efficient as a biocide than the dissociated OCl⁻. Seawater contains high concentrations of bromide ion opposite freshwater containing low concentrations and oxidizes active chlorine ion bromide to hypobromous acid (HOBr) and hypobromite ion.

Table (4). Levels of residual chlorine (mg/l) in inlet, outlet, after dosing and mixing point in front of Attaka power station during 2016-2017

Month and year	Site I	Site II	Site III	Site IV
	Inlet	After dosing hypochlorite	Outfall	Mixing Point
Nov-016	<0.1	0.51	0.18	<0.1
Dec-016	<0.1	0.28	0.18	<0.1
Jan-017	<0.1	0.22	0.11	<0.1
Feb-017	<0.1	0.11	0.05	<0.1
Mar-017	<0.1	0.13	0.08	<0.1
Apr-017	<0.1	0.22	0.10	<0.1
May-017	<0.1	0.17	0.06	<0.1
Jun-017	<0.1	0.11	0.05	<0.1
Jul-017	<0.1	0.11	0.07	<0.1
Aug-017	<0.1	0.17	0.05	<0.1
Sep-017	<0.1	0.49	0.22	<0.1
Oct-017	<0.1	0.19	0.09	<0.1
Mean		0.22	0.10	
Sum		2.71	1.24	
Mini		.11	0.05	
Max		.51	0.22	
St.def		.13	.058	

Table (5). Levels of THMs ($\mu\text{g/l}$) in inlet, outlet, after dosing and mixing point in front of Attaka power station during 2016-2017

Date	Site	Site I				Site II				Site III				Site IV			
		CHCl ₃	CHBr ₂ Cl	CHBrCl ₂	CHBr ₃	CHCl ₃	CHBr ₂ Cl	CHBrCl ₂	CHBr ₃	CHCl ₃	CHBr ₂ Cl	CHBrCl ₂	CHBr ₃	CHCl ₃	CHBr ₂ Cl	CHBrCl ₂	CHBr ₃
Nov-016		1.10	<0.1	<0.1	<0.1	<0.1	4.20	<0.1	237.25	<0.1	4.22	<0.1	59.15	<0.1	<0.1	<0.1	39.11
Dec-016		<0.1	<0.1	<0.1	<0.1	<0.1	3.11	<0.1	125.45	<0.1	3.01	<0.1	58.95	<0.1	3.14	<0.1	26.78
Jan-017		N.D	<0.1	<0.1	<0.1	<0.1	3.02	<0.1	52.39	<0.1	2.24	<0.1	48.43	1.10	<0.1	<0.1	34.19
Feb-017		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	12.16	<0.1	5.00	<0.1	31.79	<0.1	2.20	<0.1	31.00
Mar-017		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	15.34	<0.1	3.50	<0.1	15.15	<0.1	<0.1	<0.1	12.45
Apr-017		<0.1	<0.1	<0.1	<0.1	<0.1	4.01	<0.1	35.56	<0.1	4.01	<0.1	13.46	<0.1	<0.1	<0.1	8.61
May-017		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	41.29	<0.1	2.58	<0.1	56.55	<0.1	1.90	<0.1	12.34
Jun-017		<0.1	<0.1	<0.1	<0.1	<0.1	2.14	<0.1	47.58	<0.1	2.14	<0.1	44.80	<0.1	<0.1	<0.1	6.87
Jul-017		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	67.08	<0.1	3.15	<0.1	43.61	<0.1	2.24	<0.1	7.72
Aug-017		<0.1	<0.1	0.90	<0.1	<0.1	2.28	<0.1	87.16	<0.1	2.28	<0.1	62.13	<0.1	3.48	<0.1	8.45
Sep-017		<0.1	<0.1	<0.1	<0.1	<0.1	3.12	<0.1	126.75	<0.1	4.71	<0.1	40.65	<0.1	4.09	<0.1	40.00
Oct-017		<0.1	<0.1	<0.1	<0.1	<0.1	1.12	<0.1	78.75	<0.1	2.99	<0.1	33.65	<0.1	<0.1	<0.1	4.61
Mean							3.31	77.23			3.31	42.36					19.34
Sum							39.83	926.76			39.83	508.32					232.13
Mini							2.14	12.16			2.14	13.46					4.61
Max							5.00	237.25			5.00	62.13					40.00
St.def							0.97	62.65			0.97	4.73					13.70

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مصادر ومستويات التراى هالوم ثيان فى مياه جونة السويس: محطة كهرباء عتاقة (دراسة حالة)

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المستخلص

ينتج عن استخدام مادة الهيبوكلوريت في مقاومة الحشف البحري في محطات القوى الكهربائية التي تعتمد على مياه البحر في تبريد التوربينات الى تكون مركبات التراى هالوم ثيان شديدة الخطورة على البيئة البحرية في المياه الشاطئية امام هذه المحطات لذلك تم اختيار محطة كهرباء عتاقة كحالة دراسية لأنها تستخدم نفس هذه المادة في مكافحة الحشف البحري حيث تم جمع عينات مياه شهريا خلال 2016-2017 من اربع مواقع ثابتة على مدار العام وتم تحليل العناصر الآتية درجة حرارة الماء ، قيمة الرقم الهيدروجيني ، الملوحة ، المواد العضوية المؤكسدة ، الكلور المتبقي و مركبات التراى هالو مستان الأربعة واطهرت النتائج ان البروم وفورم وثنائى البرومو كلوروميثان هما الشكلين الرئيسيين من مركبات التراى هالو مستان الأربعة وقد تراوح مركب البروم وفورم بين 12.16 جزء في المليون و 237.25 جزء في المليون مع قيمة متوسطة قدرها 77.23 جزء في المليون وبإجمالي سنوي قدره 926.76 جزء في المليون ، في حين تراوح وثنائى البرومو كلوروميثان من 0.28 إلى 4.20 جزء في المليون. وقد وجد ان علاقة طردية موجبة بين مركبات التراى هالو مستان وكل من الكلور المتبقي والمواد العضوية ، في حين لوحظ ان هناك علاقة عكسية سالبة مع كل من درجات حرارة الماء وقيم الرقم الهيدروجيني هذا ولم يتم تسجيل اى علاقة بين مركبات التراى هالو مستان ودرجة الملوحة.

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