# Alkyltin and Alkyllead compounds in Coastal Water of the Suez Gulf, Egypt

# Tarek O. Said<sup>†\*</sup>, Mohamed A. Shreadah<sup>\*</sup>, Safaa A. Abd El Ghani<sup>\*</sup> and Abd El Moniem M. Ahmed<sup>\*\*</sup>

\*National Institute of Oceanography and Fisheries, Kayet Bay, Alexandria, Egypt.
 \*\*Chemistry Department, Faculty of Science, Alexandria University.
 <sup>†</sup>Correspondence author: Tarek O. Said
 E-mail: tareksaideg@yahoo.co.uk
 Fax: +2 03 4801174

Received 13<sup>th</sup> August 2009, Accepted 16<sup>th</sup> September 2009

#### Abstract

Alkyltin and Alkyllead compounds were investigated in ten stations distributed along the Suez Gulf during 2005. Gas chromatograph-flame ionization detector (GC/FID) and graphite atomic absorption spectrophotometer (GAAS) were used for the analysis to elucidate the fate of these compounds introduced to the area. In addition, total concentrations of both of tin and lead were determined using inductively coupled plasma-optical emission spectrophotometer (ICP/OES) to measure the percentage of such compounds in total metal content. High concentrations of organotin compounds (OTC) ranged from 44.2 to 82.4 ng/l were recorded; this is mainly due to major input sources and shipping activities in the Gulf area. The range of OTC concentrations in surface water exceeded the lowest toxicity thresholds for more sensitive organisms (2 ng/l). On the other hand, organolead compounds (OLC) recorded their maximum values at the middle part of the Gulf which considered as a large centers for the collection and shipment of oil from numbers of oil fields including offshore wells. Tetraethyl lead (Et<sub>4</sub>Pb) species were undetectable in most stations. However, tetramethyl lead (Me<sub>4</sub>Pb) species was predominant among alkyllead species. The results indicated that alkyllead concentrations still far below the hazards threshold (100  $\mu$ g/l).

Keywords: Alkyltin, alkyllead, coastal eater, Suez Gulf.

# 1. Introduction

The Suez Gulf is one of the main waterways in Egypt which greatly supports numerous industries that affects the Egyptian economy. The area has witnessed a development in industrial and urban activities and receives considerable amount of discharged water from different sources. Such industrial effluents amounted to about  $41 \times 10^5 \text{m}^3/\text{day}$  (El Zeky *et al.*, 2004). The major industrial activities in the Suez Gulf are oil refineries, marketing, storage and piping, fertilizers and chemicals, cement, thermal electric stations, ceramics, steel, shipyard, edible oils and fiberglass. For this, Suez Gulf is considered the most polluted area in the Red Sea.

The Suez harbor has always been an important Egyptian gate on the Red Sea since historical times. The growing activity of this harbor has led to an increasing rate of urbanization in the whole region. Suez bay (the northern part of the Suez Gulf) receives sewage and garbage both from the city of Suez and from ships awaiting transit through the Suez Canal in addition to the industrial wastes. Aquatic pollution resulting from extensive usage of organotin compounds has been of great concern due to their deleterious effects in no target organisms.

EJAR

Organotin compounds (OTC) exhibit varying degrees of toxicity towards a broad range of organisms and accordingly have been widespread applications as biocides. These compounds are persistent in the marine environment owing to their slow degradation rates and consistent flux (De Mora et al., 2003). Tributyltin (TBT) compounds have been used most extensively as the main biocide in marine antifouling paints. The ecotoxicological effects of TBT in aquatic systems have been studied in details, include gastropod imposex, mussel larvae mortality and oyster shell malformation at very low concentrations of ng/l level (Alzieu, 2000; Brancato et al., 2000; Konstantinou and Albanis, 2004). In the last few years, TBT has been considered as one of endocrine disrupter chemicals (Mensink et al., 2002; Axiak et al., 2003; Fernandez et al., 2007). Waters may be contaminated with organotin compounds by effluents from industrial plants. Further inputs to the environment result from the large-scale use of polyvinyl chloride (PVC), which contains monoand di-organotin compounds as stabilizers. Leaches

*Egyptian Journal of Aquatic Research, 2010, 36(1),33-42* 

from landfills where organotin-containing wastes are dumped may contain organotin residues, as well as municipal wastewater and sewage sludge.

On the same context, organolead compounds (OLC) have been introduced into the environment as a result of widely use of tetraalkyllead compounds as antiknock additives in gasoline. The commercially used tetraalkyllead compounds of methyl and ethyl as PbEt<sub>4</sub> and PbMe<sub>4</sub> are degraded into inorganic lead via various toxic ionic lead compounds (Noden, 1980). In spite, of increasing activities which lead to the growth pollution of organometallic compounds along the Egyptian Red Sea coasts, the effort of investigations on organometallic compounds specially organotin and organolead in the Suez Gulf is still limited and can not give us a clear picture of extent of pollution by these compounds.

Therefore, this study is aimed to determine the different forms of organotin and organolead compounds in seawater of the Suez Gulf in order to elucidate the fate of these compounds introduced to the marine environment, using the most recent advanced methods of analytical chemistry.

# 2. Materials and Methods

The Gulf of Suez (Figure 1 and Table 1) extends for about 250km southeast from the Suez Harbour in the north to Shadwan Island in the south, covering a total area of about 7500 km<sup>2</sup>. Its width fluctuates between 20 and 40 km, and its depth throughout its axis is ranged from 55 to 73 m (El-Sabah and Beltagi, 1983; El-Moselhy and Gabal, 2004). Surface seawater samples were collected seasonally from 10 stations (from I to X) covering the area of study during 2005 (Table 1 and Figure 1). Seawater samples were collected in dark glass bottles each of 2L capacity for measuring organotin and organolead compounds (OTC and OLC), and stored in the dark at 4°C. Water temperature, salinity and pH were measured in situ by using CTD equipment (YSI 600 XL, multi-parameter water quality monitor, USA). Dissolved oxygen (DO) was determined according to the classical Winkler method given by Strickland and Parsons (1975). Total suspended matter (TSM) was collected from 1L of seawater sample by filtration through washed, dried and weighed 0.45 $\mu$ m membrane filter and expressed in mg/L total suspended matter. All reagents used were of analytical grade (BDH, England and Merck, Germany), and pre-tested for possible trace metal contamination.

Dissolved metals were extracted from 1L seawater collected in acid pre-cleaned polyethylene bottles by using ammonium pyrolidinedithiocarbamate (APDC) - methyl isobutyl Ketone (MIBK) according to Eaton (1976). Analysis was carried out by using inductively coupled plasma instrument (ICP) (Spectro Analytical Instruments Gmbh, Boschstra Be 10, D-47533 Kleve/Germany, 7431/95). The particulate metals were measured according to UNEP/IAEA (1986). Total organotin compounds (tributyl tin and dibutyl tin) were determined according to Cleary and Stebbing (1987). This analysis was carried out using graphite furnace atomic absorption spectrometer (Varian GTA-96) with back ground correction.

Organolead compounds (tri-alkyllead and tetraalkyllead) were determined according to the method of Chau (1983). Analysis was carried out by using gas chromatograph/flame ionization detector (GC/FID). Two  $\mu$ L of the extracted sample were injected into GC/FID. The column used was HP-5 capillary column (30 m x 0.32 mm x 0.25  $\mu$ m); 5% diphenyl and 95% dimethyl polysiloxane, non-polar. N<sub>2</sub> was used as carrier gas at 2 ml/min flow rate. The injection and detector temperatures were held at 150°C and 200°C, respectively. The program was started at initial hold of 60°C to a final hold of 200°C at 8°C/min.



Figure 1: Sampling stations (from I to X) collected from costal water of the Suez Gulf during 2005: (I) Port Tawfiq,
(II) El Zaitiya Harbour, (III) El Kabanon, (IV) NIOF, (V) El Adabiya Port, (VI) El Sukhna, (VII) El Sukhna Harbour, (VIII) Ras Gharib, (IX) Ras Shukeir and (X) El Tour.

Name	Latitude	Longitude	Temp. (°C)	Salinity	pH (range)	DO(mg/l)	TSM
I) Port Tawfiq	29 <sup>0</sup> 57` 71"	32° 32` 46``	23.6±3.14	42.8±0.187	7.99 - 8.26	6.9±1.076	17.7±0.465
II) Zeitia Harbor	29 57 0	32 32 24	23.6±3.14	42.8±0.216	7.99 - 8.24	6.9±1.076	17.7±0.518
III) El Kabanon	29 56 46	32 29 36	23.5±3.30	42.7±0.186	7.98 - 8.21	6.9±1.076	17.6±0.514
IV) NIOF	29 55 12	32 28 24	23.4±3.39	42.7±0.206	7.90 - 8.13	8.1±1.368	19.7±2.098
V) Adabiya port	29 52 12	32 28 48	23.0±3.40	42.8±0.300	7.91 - 8.18	6.7±0.390	18.2±0.822
VI) Sukhana	29 20 24	32 36 36	23.4±3.03	42.7±0.294	8.00 - 8.22	7.1±0.486	8.9±0.807
VII) Sukhana Harbor	29 10 12	32 38 60	23.0±3.55	41.7±0.287	7.97 - 8.21	7.0±0.416	9.1±0.982
VIII) Ras Gharib	28 22 12	33 4 48	22.9±3.96	41.5±0.311	7.91 -8.09	8.2±0.804	9.8±1.710

23.1±3.49

24.1±3.38

Table 1: Average values  $\pm$  SD of physicochemical parameters measured in water of the Suez Gulf during 2005.

DO: dissolved oxygen, TSM: total suspended matter

28 8 24

28 14 24

33 16 48

33 36 36

## 3. Results and Discussion

IX) Ras Shukhrir

X) El - Tour

Table (1) illustrates the average annual values of temperature, total suspended matter, pH, salinity and dissolved oxygen at different stations in the investigated area. Averaged values of temperature showed fluctuations from  $22.9\pm3.96$  to  $24.1\pm3.38$ . Slight variations of temperature are strictly related to seasonal conditions. The average values of salinity are fluctuated between 40.3±0.519 and 42.81±0.187 which showed minor variations at different investigated stations. Suez Bay (the northwestern part of the Suez Gulf) was characterized by a slight increase in salinity as compared with those in other regions of the Suez Gulf. The relative increase in salinity of the Suez Bay is mainly accompanied with its configuration and shallowness (the mean depth is 10 m), the conveyed water of higher salinity from Suez Canal, the seasonal variation in its water level as well as the prevailing wind and cycle of heating on the Bay (Mamdouah et al., 2005).

The results declared that the pH values were always on slight alkaline side. Their absolute values showed variations between 7.91 and 8.26. The pH values registered relatively slight decrease during winter and increase during spring and summer at different investigated stations. The slight increase of pH values during spring and summer seasons may be related to the photosynthetic activity. The relative decrease of pH values during winter may be related to high solubility

of CO<sub>2</sub> in water, leading to the formation of  $HCO_3^-$ ,

and decrease of  $CO_3^{--}$  contents and pH values as mentioned by Golterman (1975).

Dissolved oxygen (DO) average concentrations varied from  $6.7\pm0.39$  mg/l at stations (V) to  $8.2\pm0.80$  mg/l at station (VIII) which indicated well oxygenated surface water at different stations. Relatively low levels of dissolved oxygen were observed at the northern part of the gulf, indicating consumption of DO for bacterial oxidation of organic pollutants and/or domestic waters from dwellings of the area (Hamed and Said, 2000).

The higher values of total suspended matter (TSM) were observed at stations I to IV (Suez Bay); while low values were generally observed at other stations.

Average TSM values were varied between  $8.9\pm0.81$  mg/l at stations V to  $19.7\pm2.09$  mg/l at station IV.

8.00 - 8.14 6.9±0.253

 $12.5\pm7.159$ 

 $9.5\pm0.336$ 

41.3±0.050 7.97 - 8.20 7.5±0.662

 $40.3\pm0.519$ 

The dissolved and particulate lead (Pb) and tin (Sn) concentrations are presented in Table (2). The average dissolved concentrations were ranged from  $2.235\pm1.3$  to  $10.483\pm2.517$  µg/l and from  $4.08\pm3.707$  to  $9.787\pm2.542$  µg/l for Pb and Sn, respectively.

Data obtained in the present study are in general comparable to those found in Suez Bay region during previous studies (Table 3). Comparison of the Pb level in present study with back ground levels in Open Ocean showed that, the Pb levels ranged from 2.25-10.48  $\mu$ g/L are generally exceeded the background level.

For dissolved tin high value of 13.72  $\mu$ g/l was measured at station (X) during summer and this may be attributed to the pleasure boats activity at El Tour during summer, revealing that dissolved inorganic tin were largely influenced by localized inputs. However, Langston *et al.* (1987) found that concentrations of dissolved inorganic tin in an enclosed harbor generally ranged from <0.005 to 0.2  $\mu$ g/l, with a very high levels up to 48.7  $\mu$ g/l were found near local pollution sources. According to Geeberg and Kingston (1983) tin concentrations in saline and sea waters are approximately 0.01 to 0.3 ng/l with values higher than 1ng/l indicative of pollution.

The average concentration of particulate lead and tin ranged from 0.295±0.302 to 1.488±2.43 µg/l and from  $0.254\pm0.428$  to  $1.709\pm1.192 \ \mu g/l$ , respectively. During winter high values of particulate Pb; 5.118 µg/l and Sn; 2.70 µg/l were measured at station II (El Zeitia Harbor). This may be due to high agitation of water and terrestrial inputs of dust particles containing metal ions during winter. In addition, station II is one of the heaviest loading and unloading operations of oil tankers in the world; moreover, it is affected by different industrial effluents from two large oil refineries (El Nasr and Suez Petroleum Companies). Minimum values of Pb; 0.003  $\mu$ g/l and Sn; 0.004  $\mu$ g/l were observed during autumn at stations II(El Zeitia Harbor) and IV(NIOF), respectively. This is may be due to the fact that water level in the bay rises sharply and also circulation of water is reversed in autumn as stated by Morcos (1970).

Stations	Dissolved			Particulate						
	Lead									
	W	SP	SU	AU	Av ±SD	W	SP	SU	AU	Av ±SD
Ι	0.65	25.70	1.79	2.89	7.76±11.99	3.09	0.27	1.26	0.01	1.16±1.39
II	3.99	0.83	2.19	2.29	2.33±1.30	5.12	0.29	0.54	0.01	1.49±2.43
III	5.32	5.36	1.59	0.65	3.23±2.46	1.00	2.36	0.00	0.34	0.93±1.04
IV	5.12	1.85	1.55	4.30	3.20±1.78	2.49	0.27	0.68	0.01	0.86±1.12
V	8.16	3.45	4.36	2.10	4.52±2.59	2.13	0.24	1.13	0.36	0.96±0.87
VI	2.52	12.49	3.48	2.44	5.23±4.86	0.27	0.64	0.89	0.77	0.64±0.27
VII	6.86	11.37	12.66	11.04	10.48±2.52	0.03	0.20	0.73	0.22	0.29±0.30
VIII	13.13	1.89	1.18	2.95	4.79±5.61	0.42	0.42	0.56	0.20	0.40±0.15
IX	3.99	7.03	5.90	2.17	4.78±2.14	2.59	0.39	0.95	0.32	1.07±1.06
Х	13.43	14.11	0.89	1.91	7.58±7.17	2.33	1.24	0.26	0.30	1.03±0.98
Tin										
	W	SP	SU	AU	Av ±SD	W	SP	SU	AU	Av ±SD
Ι	9.28	0.54	3.66	2.84	4.08±3.71	1.39	0.71	1.79	0.01	0.98±0.78
II	10.26	1.75	7.22	9.23	7.12±3.79	2.70	1.08	0.34	2.72	1.71±1.19
III	10.74	0.01	9.23	11.35	7.83±5.29	0.70	0.52	0.00	0.17	0.35±0.32
IV	10.39	1.51	1.55	8.77	5.56±4.69	0.86	0.30	0.40	0.00	0.39±0.36
V	12.74	0.02	10.63	10.68	8.51±5.75	0.53	0.49	0.01	2.13	0.79±0.92
VI	10.69	6.27	9.90	12.28	9.79±2.54	0.93	0.00	0.01	2.51	0.86±1.18
VII	9.99	0.49	6.39	8.20	6.27±4.12	2.22	0.38	1.62	0.04	1.0±1.03
VIII	9.32	1.52	13.31	6.86	7.75±4.93	0.78	0.69	0.34	0.01	0.46±0.35
IX	11.46	0.26	8.56	9.23	7.38±4.90	0.08	0.03	0.89	0.01	0.25±0.43
Х	9.26	0.60	13.72	9.13	8.18±5.48	0.66	0.11	1.86	0.01	0.66±0.85

Table 2: Average annual concentration of lead and tin  $(\mu g/l)$  in surface water of the Suez Gulf during 2005.

Av: average, SD: standard deviation

Table 3: Comparison between dissolved lead concentrations ( $\mu g/l$ ) measured in coastal surface water at the northern part of the Suez Gulf in the present study and other previous works.

Area	Range	References
Suez Bay	2.255-10.483	Present study (2005)
	3.00-6.70	Hamed (1992)
	0.43-3.10	El- Moselhy (1993)
	0.10-22.6	Abd ElAzim (1996)
	1.133-3.448	El- Moselhy et al. (1999)
	0.59-1.04	Hamed et al. (2003)
" "	1.84-2.57	El-Moselhy and Gabal (2004)
Background level	0.02-0.07 (open Ocean)	Law et al.(1994)

Generally, the distribution of metal concentrations in the Suez Gulf is affected mainly by many factors especially, the Suez Bay stations from I (Port Tawfiq) to V (Adabiya port). The water circulation in Suez Bay as well as the characteristics of water is determined by seasonal variation in water level of the Bay; high salinity of Suez Canal; variations of tides level that varies between 80cm at neap tide and 140cm at spring tide and the prevailing local winds.

Tributyltin and triphenyltin (TBT and TPhT) are ionizable, organometallic compounds that form complexes with various ligands present in the abiotic and biotic environment (Arnold *et al.*, 1997; Buck *et al.*, 2003). In water, total organotins (TBT and TPhT) exist as various neutral, non-dissociated molecules (triorganotin hydroxide (TOT-OH), triorganotin chloride (TOT-Cl)) and/or organotin cations (TOT<sup>+</sup>). Speciation of TBT depends on pH and salinity of the water. The pH of seawater is usually well buffered slightly above pH 8. At this pH the predominant compounds of both TBT and TPhT are the neutral hydroxy-complexes with >93% (Arnold *et al.* 1997). Under more acidic conditions (pH 6), the TBT-cation exists besides the neutral Tributyltin chloride (TBT-Cl) and Tributyltin hydroxide (TBT-OH) complexes (Burton *et al.*, 2005). At the conditions of the Suez Gulf, pH values suggesting that TBT and TPhT exist as neutral compounds.

Organotin compounds were determined at all stations along the Suez Gulf (Table 4). This due to the fact that the gulf is suffering from the effect of sewage discharge as well as industrial wastes from various activities such as oil refineries, fertilizer and chemical industry, power stations and loading and unloading operational inside harbors. Moreover about  $2 \times 10^8$  m<sup>3</sup> year<sup>-1</sup> are discharged from oil refineries to the Suez Bay stations from I to V (Awad, 2002). Hamed and Said (2000) stated that high concentration of dissolved hydrocarbons was found in water body of the Suez Gulf particularly at Ras Shukier oil fields (station IX) with concentration up to 9.3 µg/l. However recent studies on estimation and studying the mobility of polyaromatic hydrocarbons (PAHs) along the Egyptian Red Sea coasts revealed that the total hydrocarbon

Egyptian Journal of Aquatic Research, 2010, 36(1), 33-42

concentration ranged from 9.73 to 164.03  $\mu$ g/l with an average of 40.26  $\mu$ g/l in the Suez Gulf (Said and Hamed, 2006). OTC are adsorbed by surface active organic matter which occurs as a natural sea slick as well as by the more easily seen petroleum hydrocarbon and common in harbor waters. These natural organic sea surface films are mono molecular layers, polar in

nature, which act as sites for the accumulation of lipophilic pollutants such as chlorinated hydrocarbons and organic forms of heavy metals. So, the affinity of OTC will be enhanced by the presence of organic compounds such as petroleum hydrocarbons or oils in which they will be dissolved (US Navy, 1984).

Table 4: Concentrations of organotin compounds (ng/l as Sn) in surface water of the Suez Gulf during 2005.

Station	Winter	Spring	Summer	Autumn	Av. ±SD
Ι	45.2	49.1	82.4	60.7	59.35±16.71
II	63.3	48.7	71.4	66.3	62.43±9.74
III	77.8	44.8	49.1	58.3	57.50±14.66
IV	49.9	61.3	44.2	61.4	54.20±8.57
V	57.4	68.4	70.2	49.9	61.47±9.57
VI	81.4	49.8	58.1	55.8	61.27±13.87
VII	66.8	66.5	66.3	63.5	65.78±1.53
VIII	70.3	66.1	66.2	61.2	65.95±3.72
IX	66.6	70.3	69.1	60.1	66.53±4.55
Х	71.7	72.3	70.2	64.0	69.55±3.80
Av.±SD	65.04±11.51	59.73±10.49	64.72±11.30	60.12±4.65	62.40±4.65

Av: average, SD: standard deviation

OTC concentrations in different stations (Table 4) were ranged from  $54.20\pm8.57$  ng/l to  $69.55\pm3.80$  ng/l (as Sn). The maximum value of 80.4ng/l was recorded at station I during summer. This may be attributed to the commercial shipping activities, presence of shipyard dry dock near this station. However, the minimum value of 44.2 ng/l was recorded in station IV (NIOF) during summer indicating that this station is less affected by the sources of organotin compounds.

IPCS (1990) measured high levels of TBT in seawater, estuaries, fresh water with a maximum value of  $7.1\mu$ g/l. In addition; Harino *et al.* (1998) stated that total butyltin concentrations were ranged from 40-108ng/l in seawater from Otsuchi Bay, Japan. While, a maximum of 560ng/l of TBT was measured in seawater of Taiwan coastal areas (Lee, 2001).

The lethal TBT concentration for sensitive species is reported to be from 0.04 to 16 µg of Sn/l for short term exposures, depending on the aquatic species (WHO, 1990).while, acute effects on salt water organisms were recorded at concentrations of 1µg TBT/l. sublethal effects were observed even concentrations as low as 10ng of TBT/l (Schebek and Andreae, 1991). However, an environmental quality standard (EQS) of 20ng/l TBT for fresh water and 2ng/l for seawater has been set (UK department of the environment, 1989). It is clear from the above that the range of organotin concentration in surface water exceeded the lower toxicity thresholds for more sensitive organisms. The percentages of organotin respect to total tin (sum of dissolved and particulate form) concentrations were ranged from 0.70 to 1.17%. However, total OTC concentrations were found to have a positive insignificant correlation with total tin concentrations with r = 0.27 ( $\rho=0.05$ ; n = 8). Figure (2) shows the distribution of organotin and total tin concentrations in the different stations of the water of the Suez Gulf during the period of investigation.

Despite, organolead compounds (OLC) have high vapor pressure, low solubility in water and reactivity through photo-degradation, alkyllead compounds and their degradation products appeared in the surface waters of the Suez Gulf.



Figure 2. The relationship between the mean of OTC concentrations (ng/l) and the mean of total tin (sum of dissolved and particulate) concentrations ( $\mu$ g/l) in surface water of the Suez Gulf during 2005 (r = 0.27,  $\rho$  = 0.05).

The seasonal variations of OLC concentrations in coastal water samples from the Suez Gulf are presented in Table (5). The annual mean of tetraethyllead (Et<sub>4</sub>Pb), tetramethyllead (Me<sub>4</sub>Pb), triethyllead( $Et_3Pb^+$ ) and trimethyllead (Me<sub>3</sub>Pb<sup>+</sup>) was ranged from 0.27 to 49.61, 84.03 to 280.83, 205.18 to 1138.83 and 5.02 to 29.18 ng/l, respectively. The presence of both Et<sub>4</sub>Pb and Me<sub>4</sub>Pb indicated that leaded gasoline (used to improve the octane number of gas oil) contains either Et<sub>4</sub>Pb or methylethyllead mixture with Me<sub>4</sub>Pb. Table (5) indicated also that Et<sub>4</sub>Pb species were undetectable in most stations during different seasons; which may be attributed to the photochemical decomposition of Et<sub>4</sub>Pb in surface water and or by bioaccumulation of Et<sub>4</sub>Pb into marine organisms (Forsyth and Marshall, 1986; Krishman et al., 1988). However, the Me<sub>4</sub>Pb species 38

was abundant as a peralkylated species with ratio of 7-25% to the total OLC (sum of  $Et_4Pb$ ,  $Me_4Pb$ ,  $Et_3Pb^+$  and  $Me_3Pb^+$ ) while the ratio of  $Et_4Pb$  to the total OLC was 0.04-14%. This suggested that not only leaded gasoline was the source of  $Me_4Pb$  in the environment but also chemical alkylation of Pb(II) to produce  $Me_4Pb$  and ionic methyllead compounds may occur (Forsyth and Marshall, 1986). In addition, methylated OLC are more volatile, more stable and less toxic than  $Et_4Pb$ .

Figure (3) showed the distribution of average concentrations of OLC along the Suez Gulf. It is clear

that among four species of OLC,  $Et_3Pb^+$  was the most dominant compound with the range between 63% and 89% of total OLC. This due to the fact that, trialkyllead is the most stable product of peralkylated degradation with a half life of a few days in the photic zone to up to one year in the dark, which in turn decomposes further to inorganic lead (Mika *et al.*, 2001).

Table 5: Concentrations of Et <sub>4</sub> Pb, Me <sub>4</sub> Pb, E	<sub>3</sub> Pb <sup>+</sup> and Me <sub>3</sub> Pb	+ (ng/l) in coastal	surface water	of the different stations
of the Suez Gulf during 2005.				

Stations	Winter	Spring	Summer	Autumn	Av.		
Ι	ND	ND	ND	67.38	16.85		
II	ND	142.89	ND	ND	35.72		
III	ND	177.61	ND	ND	44.40		
IV	96.35	90.77	ND	ND	46.78		
V	ND	ND	1.07	ND	0.27		
VI	ND	45.20	0.23	ND	11.36		
VII	ND	161.77	0.21	ND	40.49		
VIII	198.37	ND	0.09	ND	49.61		
IX	ND	ND	1.11	ND	0.28		
Х	98.41	ND	0.58	ND	24.75		
mean	393.13	618.24	3.29	67.38	270.51		
Me <sub>4</sub> Pb							
Ι	124.88	136.67	129.84	179.91	142.82		
II	87.97	100.93	125.81	136.86	112.89		
III	141.53	189.48	255.18	134.86	180.26		
IV	119.88	99.15	ND	177.77	99.20		
V	138.85	125.02	ND	189.95	113.45		
VI	174.61	ND	253.33	ND	106.98		
VII	114.97	142.01	138.24	728.09	280.83		
VIII	127.01	ND	96.25	118.46	85.43		
IX	105.19	124.15	196.57	139.46	141.34		
Х	73.78	131.82	130.53	ND	84.03		
mean	1208.67	1049.23	1325.75	1805.36	1347.23		
$Et_3Pb^+$	•	•	•	•	•		
I	474.26	ND	1323.87	604.16	600.16		
II	117.00	ND	917.16	96.19	282.58		
III	ND	1442.31	ND	297.22	434.88		
IV	344.79	ND	ND	775.37	280.04		
V	1409.23	728.37	ND	54.35	547.24		
VI	530.27	400.09	ND	710.66	410.26		
VII	641.55	296.87	1741.59	710.47	847.62		
VIII	141.88	522.68	97.42	58.75	205.18		
IX	733.48	1440.97	1086.71	690.85	988.00		
Х	450.26	1234.36	1228.76	1641.95	1138.83		
mean	4842.72	6065.65	6395.51	5639.97	5734.79		
Me <sub>3</sub> Pb <sup>+</sup>							
Ι	38.73	ND	ND	3.79	10.63		
II	9.60	15.91	ND	30.55	14.02		
III	ND	30.80	ND	29.49	15.08		
IV	9.44	10.64	ND	ND	5.02		
V	31.00	ND	ND	5.95	9.24		
VI	47.53	4.40	11.51	53.24	29.18		
VII	30.10	27.19	ND	45.27	25.65		
VIII	31.26	ND	3.68	ND	8.74		
IX	30.38	0.99	ND	ND	7.85		
Х	14.29	31.96	ND	46.34	23.15		
mean	242.33	121.89	15.19	214.63	148.56		

ND: below detection limit.



Figure 3: The average concentrations of OLC species (ng/l) in surface water of the Suez Gulf during 2005.

In general, the maximum values of OLC recorded in the water of the Suez Gulf were 198.37, 728.09, 1751.59 and 53.24ng/l for  $Et_4Pb$ ,  $Me_4Pb$ ,  $Et_3Pb^+$  and  $Me_3Pb^+$ ; respectively. These values were observed at stations VI, VII and VIII (the middle part of the Gulf), which considered as a large centers for the collection and shipment of oil from numbers of oil fields including offshore wells. Consequently, a significant part of organic lead is derived from non-combustion gasoline spilled into the gulf during maritime activities and from coastal gasoline stations in which all lead is in the form of tetraalkyllead compounds. Insignificant correlation of r = 0.51 ( $\rho = 0.05$ , n = 8) was found between the average concentrations of OLC and lead (Figure 4). Maddock and Taylor (1980) considered the level of alkyl lead 100µg/l represent the seawater concentration threshold above which irreparable damage to aquatic organisms may occur. In coastal water of the Suez Gulf, alkyllead concentrations did not reach this limit, indicating that these compounds are, for the time being, still far below the hazardous threshold.



Figure 4: The relationship between total lead concentrations and OLC at different stations of the Suez Gulf during 2005 (r = 0.51,  $\rho = 0.05$ ).

## References

- Abd El-Azim, H.M.: 1996, Lead dynamics in Suez Bay. MSc. Thesis, Faculty of Science, Helwan University, 124 pp.
- Alzieu, C.: 2000, Environmental impact of TBT: the French experience. *Sci. Total Environ.* 258, 99–102.
- Arnold, C.G., Weidenhaupt, A., David, M.M., Mu ller, S.R., Haderlein, S.B. and Schwarzenbach, R.P.: 1997, Aqueous speciation and 1-octanol-water partitioning of tributyl- and triphenyltin: effect of pH and ion composition. *Environmental Science* and Technology 31, 2596–2602.
- Awad, F.K.: 2002, Characterization and determination of the environmental wastes of Suez province. PhD Thesis, Faculty of Science, Mansoura University, 157pp
- Axiak, V., Micallef, D., Muscat, J., Vella, A. and Mintoff, B.: 2003, Imposex as biomonitoring tool from marine pollution by tributyltin: some further observation. *Environmental International*, 28: 743-749.
- Brancato, M.S., Cardwell, R.D. and McKay, S.: 2000, Chambering in the Pacific oyster, Crassostrea gigas, and its relationship to tributyltin. *Mar. Environ. Res.* 50 (1–5), 437.
- Buck, B., Mascioni, A., Que Jr., L. and Veglia, G.: 2003, Dealkylation of organotin compounds by biological dithiols: toward the chemistry of organotin toxicity. *Journal of American Chemical Society* 125, 13316–13317.
- Burton, E.D., Philips, I. R. and Hawker and D.W.: 2005, In situ partitioning of butyltin compounds in estuarine sediments. *Chemosphere* 59, 585–592.
- Chau Y.K.: 1983, The determination of dialkyllead, trialkyllead, teraalkyllead and lead (II) ions in water by chelation/ extraction and gas chromatography/ atomic absorption spectrometry. *Analytica Chemica Acta*, 146: 211-217.
- Cleary, J.J and Stebbing, A.R.D.: 1987, Organotin in the Surface Microlayer and Subsurface Waters of Southwest England. *Marine pollution*, 18: 238-246.
- De Mora, Scott W. Fowler, Roberto Cassi and Imma Tolosa: 2003, Assessment of organotin concentration in marine sediments and biota from the Gulf and adjacent region. *Marine Pollution Bulletin*, 46:401-409.
- Eaton A.: 1976, Marine geochemistry of cadmium. *Marine chemistry*, 4: 141-1154.
- El- Sabah, M.I. and Beltagi, A.I.: 1983, Hydrography and chemistry of the Gulf of Suez during September 1966. *Bulletin National Institute of Oceanogeraphy and Fisheries. Egypt*, 9: 78-82.
- El-Moselhy, Kh. M.: 1993, Studies on the heavy metals level in some economic fishes in the Suez Gulf. MSc. Thesis, Faculty of Science, El-Mansoura University.

- El-Moselhy, Kh.M. and Gabal, M.N.: 2004, Trace metals in water, sediments and marine organisms from the northern part of the Gulf of Suez, Red Sea. *Journal of Marine System*, 46: 39-46.
- El-Moselhy, Kh.M., Diab, A.A., Tolba, M.R. and Mohamadein, L.I.: 1999, Levels of some heavy metals in coastal water, sediment and the limpet *Patella* sp. from the northern part of the Gulf of Suez (Suez Bay). Egypt. *Journal of Aquatic Biology and Fisheries*, 3: 69–84.
- El- Zeky, A., M., Shalaby, S., E., Harmed, M., S. and Mohamed, A.: 2004, National Program of Action (NPA) for the protection of the Marine Environment from Land- Based Activity within the Rea Sea Area in Egypt, Suez Governorate, pp. 103.
- Fernandez, M.A., Pinheiro, F.M., de Quadros, J.P. and Camillo, E.: 2007, An easy, non- destructive, probabilistic method to evaluate the imposex response of gastropod populations. *Marine Environmental Research*. 63: 41-54.
- Forsyth, D.S. and Marshall W.D.: 1986, Ionic Alkyllead in Herring Gulf from the Great Lakes Region. *Environmental Science and Technology*, 20: 1033-1038.
- Geeberg, R.R. and Kingston, H.M.: 1983, J. Anal. chem, 55, 116.
- Golterman, H.L.: 1975, Physiological Limnology, Elsevier Publishing Co. Amsterdam.
- Hamed, M.A.: 1992, Sea water quality at the northern part of the Gulf of Suez and the nearby area of Suez Canal. MSc. Thesis. Faculty of Science. Mansoura University. pp.80.
- Hamed, M.A. and Said, T.O.: 2000, Effect of pollution on the water quality on the Gulf of Suez. *Egyptian Journal of Aquatic Biology and Fisheries*, 4: 161-178.
- Hamed, M.A.; Said, T.O. and Nassar, M.Z.: 2003, Effect of heavy metals and aromatic hydrocarbons on phytoplankton biomass as represented by chlorophyll-a in the northern part of the Suez Gulf. *Journal of Egyptian Academic Society for Environmental Development*, (D-Environmental studies), 4: 67-85.
- Harino, H., Fukushima, M., Yamaoto, Y., Kawai, S. and Miyazaki, N.: 1998, Contamination of butyltin and phenyltin compounds in the marine environment of Otsuchi Bay, Japan. *Environmental Pollution*, 101: 209-214.
- IPCS: 1990, Tributyltin compounds. International Programme on chemical safety (Environmental Health Criteria 116). World Health Organization, Geneva.
- Konstantinou, I.K. and Albanis, T.A.: 2004, Worldwide occurrence and effects of antifouling paint booster biocides in the aquatic environment: a review. *Environ. Int.* 30: 235–248.
- Krishman, K., Marshall, W.D. and Hatch, I.: 1988, Ionic alkylleads in salt marsh periwinkles (*Littorina*

*irrorata*). *Environmental Science and Technology*, 22: 806-811.

- Langston, W. J. and Burt, G. R.: 1987, Tin and organotin in water, sediment, and benthic organisms of Poole Harbor. *Marine Pollution Bulletin*, 18: 634-639.
- Law, R.J., Waldock, M.J., Allchin, C.R., Laslett, R.E. and Bailey, K.J.: 1994, Contaminants in seawater around England and Wales: results from monitoring surveys, 1990–1992. *Marine Pollution Bulletin*, 28: 668–675.
- Lee, C.C.: 2001, The establishment of the environmental distribution survey of toxic chemicals. A Research Report, EPA. 90-U1 J1-02-104, Environmental Protection Agency. Taiwan.
- Maddock, B.G. and Taylor, D.: 1980, The acute toxicity and bioaccumulation of some lead alkyl compounds in marine animals, In: Branica, M. and Konrad, Z. (eds.), Lead in the Marine Environment, pp. 233–261, Pergamon, Oxford.
- Mamdouh, A.F., Shreadah, M.A., Aboul Soeud, A., Abdel Rahman, S.M. and Shindy, M.: 2005, Hydrography and chemical characteristics of the coastal water along the Gulf of Suez. *Egyptian Journal of Aquatic Research*, 31: 1-14.
- Mensink, B.P., Krault, H., Dick Velhoak, A., ten Hallers- Tjabbes, C.C., Koerman, J.H., Van Hattun, B. and Boon, J.P.: 2002, Imposex induction in laboratory reared Juvenile Buccinum undatum by tributyltin (TBT). *Environmental Toxicology and Pharmacology*, 11: 49-65.
- Mika, N., Branica, M. and Harrison, R.M.: 2001, Total and organic lead distribution in water, sediment and organisms from the Eastern Adriatic Coast. *Chemical Speciation and bioavailability*, 13: 121-128.
- Morcos, S.A.: 1970, The tidal currents in the southern part of the Suez Canal. Helsiniki, Finland, 51-307.
- Noden, F.G. 1980, The determination of tetraalkyllead compounds and their degradation products in natural waters. In *Lead in the Marine Environment*, ed. M. Branica & Z. Konrad. Pergamon Press, Oxford, pp. 83-91.
- Said, T.O. and Hamed, M.A.: 2006, Mobility of polycyclic Aromatic Hydrocarbons in water of the Egyption Red Sea Coasts. Bulletin of Environmental Contamination and Toxicology, 77: 126-136.
- Schebek, L. and Andreae, M.: 1991, Methyl- and Butyl compounds in water and sediments of the Rhine River. *Environmental Science and Technology*, 25: 871-878.
- Strickland J.D.H. and Parson T.R.: 1975, A practical Handbook of Sea Water Analysis. *Bulletin of Canadian fisheries and Research*, 311P.
- UNEP/IAEA: 1986, References methods for marine pollution studies, 39.

Egyptian Journal of Aquatic Research, 2010, 36(1), 33-42

- United Kingdom department of the environment: 1989, water and the environment. London, UK Department of the environment p. 26 (circular No 7/89).
- US Navy: 1984, Environmental assessment of fleet wide use of organotin antifouling paint. US Vaval Sea Systems Command, Washington, D.C., USA.
- WHO: 1990, Organo Tin and its derivatives environmental aspects. *Environmental Health Criteria*, no. 85, World Health Organization, Geneva.

مركبات القصدير والرصاص العضوية في المياه الساحلية لخليج السويس طارق عثمان سعيد، محمد عطيه شريدح، صفاء عبد السلام عبد الغني، عبد المنعم محمد أحمد

تمت دراسة مركبات القصدير والرصاص العضوية بعشرة محطات موزعة على ساحل خليج السويس خلال 2005م. تم إستخدام جهاز كروماتوجرافيا الغاز وجهاز الإمتصاص الذرى فى تحليل وتحديد مصادر تلك المركبات بمنطقة الدراسة. بالإضافة فقد تم إستخدام وحدة جهاز البلازما الحثية المزدوجة فى قياس المحتوى الكلى للقصدير والرصاص وإستخدامها فى حساب نسب المركبات العضوية بالعينات المجمعة. تم رصد تركيزات عاليه من مركبات القصدير العضوية تراوحت فيما بين 2و44 إلى 4و28 نانوجرام/لتر نسبة إلى أنشطة المراكب القائمة فى خليج السويس. تخطت مستويات القصدير العضوية الحد القليل المؤثر على الكائنات الحية المراكب القائمة فى خليج السويس. تخطت مستويات القصدير العضوية الحد القليل المؤثر على مستوى لها بوسط الخليج والذى يعتبر مركز كبير لعمليات الشحن والتفريغ لزيت البترول بداخل حقول البترول الواقعة بعيداً عن الشاطىء. كما سجلت مركبات رابع ميثيل الرصاص العضوية أعلى بمنور البترول بداخل حقول مركبات رابع إيثيل الرصاص، حيث أن الأخير لم يتم رصده فى معظم المحطات، بينما لم تتخطى مستويات مركبات الرماص العضوية المريات القلمي .