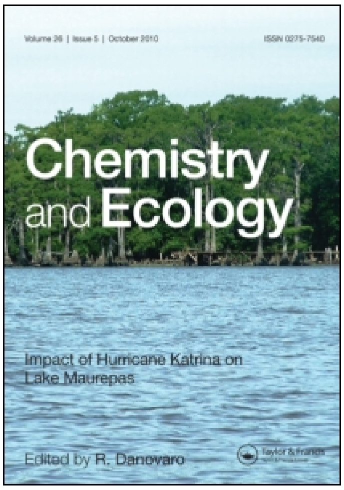

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Tributyltin pollution in sediments from Alexandria's coastal areas

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Presence of Tributyltin (TBT) in Alexandria's coastal water areas has been demonstrated by measuring concentrations of this compound. The TBT was measured in sediments from three docking areas namely: Western Harbour, Eastern Harbour and Abu Qir Bay. The sediment of those areas has been affected by marine traffic and other industrial activities. This is reflected by the distribution of TBT in the sediments nearby the shipyards in the three docking areas of the region where the average values of 258.6 ηg TBT/g for Western Harbour; 126.4 ηg TBT/g dw for Abu Qir Bay and 42.3 ηg TBT/g dw for the Eastern Harbour were recorded. This fact reflects the effect of industry and marine traffic on the marine environments of the Alexandria region.

Keywords: Tributyltin; Pollution; Sediments; Egypt

1. Introduction

Tributyltin (TBT) is an organotin used in marine environments as a toxic agent in antifouling paints over the past two decades [1, 2]. High concentrations have frequently been found in water, biota and sediment in the vicinity of marinas and yacht ports implying that antifouling paints applied to boats, ships and docks are a major source of TBT in aquatic environment. A series of studies have shown that TBT is highly toxic toward various marine organisms [3–6]. To prevent the destruction of marine ecosystems, usage of antifouling paints on boats less than 25 m in length and fish equipment have been banned or regulated in developed nations since the late 1980s [1, 2, 7]. Nevertheless, significant concentrations of TBT are still high (1–2 ηg TBT l^{-1}) as reported by Gibbs *et al.* [8], Davies *et al.* [9] and Alzieu [10]. Furthermore, the International Maritime Organization (IMO) has repeatedly expressed concern about the detrimental effects of TBT-based antifouling paints on non-target marine organisms. Consequently, in November 1999, based on a conviction over the ecotoxicological impacts of TBT, a resolution was approved by the Marine Environmental Protection Committee proposing a global prohibition on the application of organotin compounds as biocides in antifouling systems on ships by January 1, 2003, and a complete prohibition of its presence by January 1,

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2008 [11, 12]. Although, many studies have been conducted on TBT and in few cases, its derivatives in sediment samples, there is still a general lack of information on levels in water and sediments, and fate and effects on local organisms inhabiting the coastal water of Egypt. There have not been any studies conducted on TBT in the south eastern Mediterranean along Egyptian coastal waters, except those undertaken by Aboul El-Dahab [13, 14]. The aim of this work is to provide recent data on the occurrence and comparison of TBT in surface sediments from three hot spots along Alexandria coastal areas which are subjected to different types of discharges.

2. Materials and methods

The region of Alexandria is burdened with heavy marine traffic as well as marine related industrial activities. Three hot spot sites were visited namely, Western Harbour, (the major commercial harbour); Eastern Harbour (small fishing harbour) and Abu Qir Bay (an ecologically important Bay) as showing in table 1. Alexandria Western Port is the largest commercial port in Egypt where about 70% of the Egyptian foreign trade is served. Exporting and importing activities of raw materials, general foods, fertilizers, cement, grains, coal, oil, molasses and petroleum are served at the Western Port. Different types of ships, carriers, submarines, containers, tugboats, and floating docks use the port for various purposes. The other two areas are mainly fishing areas. Eastern Harbour, a semi-closed basin, is affected by untreated sewage [15]. Most of the ships used in Eastern Port are fishing boats, yachts and leisure boats. Abu Qir Bay receives various types of continental discharges. It receives agricultural as well as industrial waste from textile factories, paper companies and urea fertilizer. The bay is also affected by the power station and the facilities of El-Timsah ship building company [16]. The stations in this study encompass the influence of both commercial and naval vessels, repair facilities, fishing boats and also leisure vessels where their source term for TBT entering the water is high. Table 1 and figure 1 show the sampling sites in the present study.

Sediment samples were collected from 16 locations by means of Peterson grab samples from depths ranging between 5 and 25 m. Approximately the top 2 cm of sediments were

Table 1. Location and site number of collected sediment samples.

Location	Site	Latitude	Longitude	Position description
Abu Qir Bay	1	31° 16′ 35.4″N	30° 10′ 37.3″E	Outside port
	2	31° 19′ 26.8″N	30° 04′ 52.2″E	Vessels anchorage area
	3	31° 19′ 04.4″N	30° 04′ 28.8″E	In front of Temssah port
	4	31° 19′ 81.1″N	30° 04′ 35.0″E	Traffic pathway, inside port
	5	31° 16′ 24.4″N	30° 09′ 27.8″E	In front of Petrojet Port
Western Harbour	6	31° 09′ 49.5″N	39° 50′ 25.5″E	Anchorage area, out side port
	7	31° 10′ 26.0″N	30° 52′ 12.9″E	Dry dock (the old one)
	8	31° 16′ 26.4″N	29° 04′ 41.0″E	Dry dock (the new one)
	9	31° 11′ 26.4″N	29° 52′ 21.2″E	Traffic pathway, inside port
	10	31° 11′ 38.3″N	29° 52′ 39.7″E	In front of passengers station
	11	31° 11′ 51.7″N	29° 52′ 25.0″E	In front of Egyptian ship
	12	31° 11′ 54.2″N	29° 52′ 48.1″E	In front of Alex. dry dock
Eastern Harbour	13	31° 10′ 33.5″N	29° 49′ 26.2″E	Vessels anchorage area
	14	31° 12′ 53.2″N	29° 54′ 12.5″E	Entrance of Eastern port
	15	31° 12′ 40.9″N	29° 53′ 08.2″E	Fishing boat area
	16	31° 12′ 37.5″N	29° 53′ 01.5″E	In front of private slipway

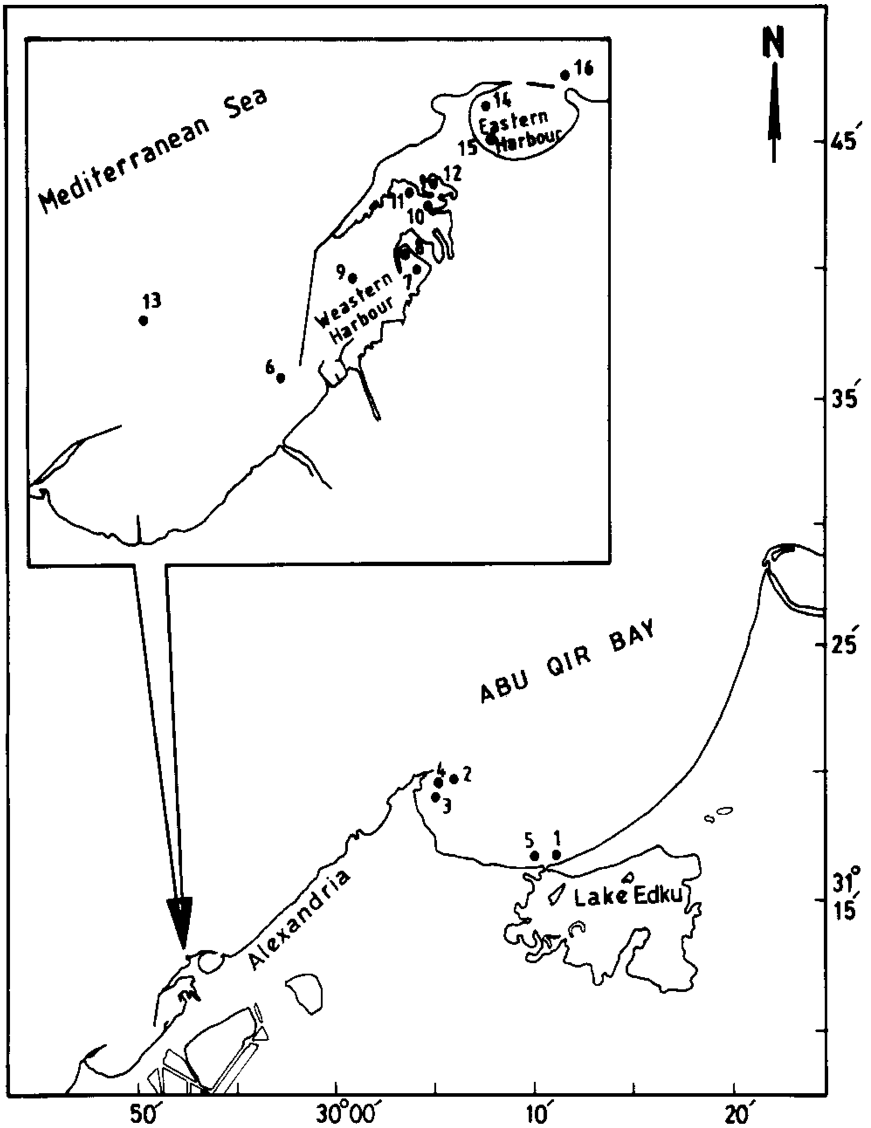

Figure 1. Map of sample locations.

removed by a stainless steel spoon and stored in a labeled screw caped glass jar and kept refrigerated until preparation for analysis. All glassware was washed with nitric acid and deionized water before use and heated at 450 °C overnight. Sediment sub-samples were taken for the determinations of organic carbon (OC), water content, $CaCO_3$ and grain size distribution according to Folk [17].

TBT determination was carried out according to the method described by Tsuda *et al.* [18]. The wet sediment samples were extracted with hexane following acid leaching with HCl. After centrifugation, aliquots of organic layers were evaporated to near dryness and residues were dissolved in ethanol prior to hydride derivatization. Clean up was achieved by column chromatography using silica gel and GC with electron capture detector (ECD) which was employed for quantization.

Table 2. Recovery study (certified reference material PACS-2).

Element	Certified concentrations (μg/g dw)	Concentration found (μg/g dw)	Recovery
TBT	885.6	904 ± 86	98.71%
	922.5		
	892.5		
	895.7		
	865.8		
Mean ± SD	892.4 ± 20.4		

Note: Number of replicate samples is five.

A SHIMADZU 17A gas chromatography equipped with Ni^{63} electron capture detector-GC column 30 m × 0.251 mm – AT – 50 capillary column was used for this study. The column temperature was kept at 120 °C for 2 min before the temperature was increased at 220 °C at 10 °C min^{-1}. Detector temperature was maintained at 25 °C and the injection part at 250 °C. The carrier gas was Helium (40 ml min^{-1}) and the split ratio 10. The volume of TBT extract injected was 5 μl. Quantification was based on the retention times and the peak height of the external standards. All results reported in this study are expressed as ηg TBT g^{-1} dry wet basis. The whole analytical procedure for each sediment was validated by analyzing a standard reference material PACS-2 (NRCC, Canada) as shown in table 2.

3. Results and discussion

The results of determination of the water content, total organic carbon (TOC), carbonate content and particle size composition as well as the TBT content in surface sediment samples for the Western Harbour, Eastern Harbour and Abu Qir Bay are reported in table 3.

Table 3. Levels of TBT (ηg TBT/g dw) in the surface sediment collected from the area of study.

Location	Site	Water content (%)	Organic carbon (%)	$CaCO_3$ (%)	Grain size		TBT (ηg/g) dry wt
					Sand (%)	Silt (%)	
Abu Qir Bay	1	21.63	2.37	11.78	85.57	14.43	30.34
	2	24.22	1.61	12.50	78.59	21.41	12.03
	3	50.96	3.96	32.42	19.75	80.25	393.69
	4	44.48	7.06	32.56	67.89	23.11	168.02
	5	22.96	1.37	12.79	82.22	17.78	27.84
Western Harbour	6	31.43	1.85	66.13	94.04	5.96	52.92
	7	38.10	6.60	67.81	84.55	15.75	101.30
	8	18.93	1.70	91.06	100.00	0.00	111.03
	9	20.15	3.37	86.85	92.91	7.09	558.05
	10	33.29	4.44	37.25	44.79	55.21	334.37
	11	20.20	8.72	74.88	96.61	3.33	293.69
	12	26.34	1.76	12.66	90.00	10.00	358.97
Eastern Harbour	13	13.93	1.46	41.62	100.00	0.00	84.16
	14	12.27	1.87	93.19	100.00	0.00	23.69
	15	25.49	2.32	91.40	96.55	3.45	51.39
	16	37.58	2.53	22.39	85.56	14.44	51.91

Single values are mean concentrations (on a dry weight basis) of two independent samples.

The water content is an important factor in controlling the early digenetic processes of sediments. It affects the rate of reaction, in particular, the oxidation-reduction process, the pH and the amount of TBT that can trapped due hydrophilic character. The average water content was varied from 25.1% in sediment from the Eastern Port, 32.9% in sediment from Abu Qir Bay and 26.9% in sediment from Western Harbour.

The percentages of total organic carbon (TOC) in the sediment samples from different localities are given in table 3. TOC in the sediments reflects the high productivity of water column that contributes organic detritus to bottom sediments. It also, reflects terrestrial inputs from land-based sources like river runoffs, industrial waste sewage in flows and agricultural drains.

The distribution pattern of total organic carbon in the three areas under investigation was varied. In Abu Qir Bay sediments, the highest concentration of TOC (7.1%) was found at station 4 in the traffic pathway while the minimum amount (1.4%) was found at station 5 in front of Petrojet Port reflecting the low effect of its waste on the TOC%. The lowest value of TOC% in Western Harbour was recorded at station 8 while its highest values were observed at stations 7 and 11. This was attributed to the dumping of used material from the cleaning operations into the sea. The lowest average value of TOC% recorded at Eastern Harbour was attributed to the low amount and nature of the discharged waste compared to that dumped in Abu Qir Bay and Western Harbour, where it is mainly sewage discharge in the former but industrial and agricultural waste that remains from the maritime activities in the others.

Results for TBT concentrations in the surface layer of the sediments from the regions showed interesting patterns in the different areas. The results are given in table 3. The average concentrations in the Western Harbour was the highest 258.7 ηg TBT g^{-1} compared with an average of 126.4 ηg TBT g^{-1} for Abu Qir Bay and 42.3 ηg TBT g^{-1} for the Eastern Harbour. The concentrations of TBT in sediments reflect more correctly the actual local inputs of this material in different areas. In Abu Qir Bay, station 3 recorded the highest concentration of TBT (393.7 ηg/g), close to El-Temssah shipyard company followed by station 4 (168.0 ηg/g) which is attributed to the traffic path of the ships inside the port.

The distribution of TBT in the Western Harbour showed that the highest concentration was recorded at station 9 (558 ηg/g) reflecting the high activities of ships in the port using antifouling paints followed by stations 11 and 10 where ships are being built and repaired, and in front of the passengers port respectively.

In the Eastern Harbour, the highest concentration was observed near the anchorage area outside the port at station 13, while values recorded near at El-Boughaz and the fishing boat slipway inside the port ranged between 23 and 51 ηg/g.

The concentrations of TBT in the present study are relatively lower than those reported by Abou El-Dahab [13], 275–1275 ηg/g for Western Harbour; 190–265 ηg/g for the Eastern Harbour and 155–300 ηg/g for Abu Qir Bay. The trend, however, seems to be quite similar, concentrations decrease but the levels remain quite high. Comparison with previous studied of Mediterranean Sea, revealed that the average level of TBT along the Alexandria coastal area in the present work is lower than that reported by Tselentis *et al.* [19] for sediment along Greek Coastal sites (1400 ηg/g dry wt) but comparable to that reported by Gomez-Ariza *et al.* [20] for sediment along the Spanish Coast (195 ηg/g dry wt).

The present work reveals the occurrence of TBT in the surface sediments of the Alexandria area and provides recent data on its occurrence. The concentration of TBT is mainly related to shipyards, ship-repairing dockyards and marinas in the area. Efforts should be made especially in the Western Harbour to reduce the presences of TBT in the sediments as these activities increase.

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