

Organotin compounds in Egyptian Mediterranean sediments

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Abstract

Determination of butyltin compounds were investigated at 39 stations distributed along the Egyptian Mediterranean Sea-coast during summer 2008. Gas chromatography-electron capture detector (GC/ECD) was used for the analysis to elucidate the fate of these compounds introduced into the area. Total concentration of tin was determined using graphite furnace atomic absorption spectrophotometer (GAAS). Tributyltin (TBT) was the predominant species with an average concentration of 2.29 and 3.74 µg/g dry wt. for the eastern and western sectors, respectively, reflecting recent input of TBT into the area of study. Dibutyltin (DBT) was not detected at most stations. A significant positive correlation ($r = 0.36$, $P = 0.05$) was computed between TBT and total tin (ΣSn), implying considerable anthropogenic input of butyltin compounds to total tin contamination levels. The percentages of TBT were ranged from 0.87-55.31% and from 0.17-18.39% for the eastern and western sectors, respectively. This could be attributed to heavily shipment activities in the western sector where TBT was used as antifouling paints. The present study revealed higher concentration of TBT than the highest trigger value (70 ng/g), suggesting a threat to benthic biota of the region. According to the concentration of TBT, sediments were classified as highly- grossly contaminated.

Keywords: Tin, tributyltin, sediment, Mediterranean Sea coast, Egypt

1. Introduction

Due to the wide industrial applications, considerable amounts of organotins have entered various ecosystems (Hoch, 2001). OTC exhibit varying degrees of toxicity towards a broad range of organisms and accordingly have been widespread applications as biocides. Uses of OTCs include fungicides, miticides, molluscicides, nematocides, ovicides, rodent repellants, wood preservatives and antifouling paints, primarily containing tributyl-, triphenyl- and tricyclohexyltin as toxic additives (Bennett, 1996). These compounds are persistent in marine environment owing to their slow degradation rates and consistent flux (de Mora *et al.*, 2003).

So far attention has mainly given to TBT pollution in water and sediments because of its high toxic effect to aquatic life even at very low concentration (Chagol *et al.*, 1990). TBT among OTC is of the most concern due to its direct introduction into the environment, its high toxicity towards “non-target” organisms (oysters and mussels), embryonic and larval organisms (Bryan and Gibbs, 1991; Konstantinou and Albanis, 2004; Antizar-Ladislao, 2008) and its bio-accumulation causes environmental and economic damage around the

world (De Carvalho Oliveira and Santelli, 2010). 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). Although many countries have restricted the use of highly toxic OTC following the recommendation of International Maritime Organisation (IMO, 1989), and forced the development of national regulations in many countries, their use is far from being eliminated entirely. Thus, these harmful substances will represent a risk for aquatic and terrestrial ecosystem, for some time to come. Therefore, a continued research on elucidating the pathways and persistence of these pollutants in natural system is required.

Up to the recent years a few studies (Shreadah *et al.*, 2006) are known about the distribution of organotin compounds in sediment along the Egyptian Mediterranean coast.

Therefore, this study aimed to provide recent data on the occurrence and distribution of organotin compounds in sediments of the Egyptian Mediterranean Sea coast as a first record for their environmental impact.

2. Material and methods

2.1. Study area

The Mediterranean Sea lies between Europe, Asia and Africa continents and without the Black Sea covers about 2.5 million km², with an average depth of about 1500 m and a volume of 3.7 million km³. The maximum length of the Mediterranean Sea from Gibraltar to Syria is about 3800 km and the maximum distance in north-south direction from France to Algeria about 900 km, yet one is never further than 370 km from the coast, and most often, considerably less, with more than half of the Mediterranean Sea being less than 100 km from the coast (UNEP, 1990).

The western coast of the Egyptian Mediterranean Sea extends from the Gulf of El- Salloum to Agami head land, comprising the northern margin of the western desert. The population of this sector is very sparse and the activities of local people are limited to grazing and small scale agriculture. However, the east coast extends from the Eastern Harbor to El-Arish.

The area of study is divided into two main sectors: i) The eastern extends from El-Arish to the eastern harbor, ii) The western extends from El- Salloum to El-Mex (Table 1, Figure 1b).

2.2. Sampling and analysis

Thirty nine sediment samples were collected along the Egyptian Mediterranean coast; 22 of them were collected from the eastern sector and 17 from the western one. The samples were collected using a Hydro-Bios stainless-steel grab sampler on R/V Salsabeel belonging to the National Institute of Oceanography and fisheries during summer 2008 (Table 1, Figure1). The samples were divided into two sub-samples; one for determination of organotin, placed in polypropylene bottles and the second one for determination of total tin, placed in pre-cleaned plastic bags. All samples were kept frozen at -20°C until analysis. Once in the laboratory the sediment samples were freeze-dried by using Freeze-dried (Labconco, England), grinding with agate mortar and stored at room temperature.

For total tin analysis, an exact weight (0.5 g) of dry sediment sample was completely digested in Teflon vessels using a mixture of HNO₃, HF and HClO₄ (3:2:1) at 70°C (UNEP/IAEA, 1986). The final solution was diluted to 25 ml with double deionized distilled water. All digested solutions were analyzed in duplicate using an atomic absorption spectrometer (AAS Shimadzu Model AA 6800 equipped with a Graphite furnace automizer GFA-EX7) and the results were expressed in µg/g; dry weight. Conditions for GFA-EX7 obtained for tin applying AAS instrument were as follows, the absorption wavelength was 286.3 nm, Slit width was 0.5, ashing temp was 400°C, Atomizing temp was 2500°C, Graphite tube was pyrolytic and detection limit was 2 ng/g. All reagents used were of analytical grade (Merck). For quality control (QC) and quality assurance (QA), replicates were analyzed under

the same procedures mentioned above. A standard reference material (IAEA-356, marine sediment; Analytical Quality Control Services, Austria) was also digested and analyzed similarly to ensure the quality control and accuracy of the analysis. Analytical results of the quality control samples indicated a satisfactory performance of tin determination within the range of certified values with 90.4-97.5% recovery.

Table 1: Sampling locations at the investigated area during 2008

St.	Name	Latitude			Longitude		
		°	'	"	°	'	"
1	El-Arish 1	31°	11'	20"	33°	50'	14"
2	El-Arish 3	31	15	55	33	50	14
3	Sahl El Tina 1	31	10	6	32	29	49
4	Sahl El Tina 3	31	21	8	32	29	31
5	Damietta 1	31	34	55	31	39	52
6	Baltim 1	31	38	18	31	20	4
7	Baltim 3	31	47	11	31	20	4
8	Gamasa 1	31	38	36	31	6	40
9	Gamasa 2	31	41	40	31	6	40
10	Gamasa 3	31	46	34	31	6	3
11	Burullus 1	31	36	27	30	51	26
12	Burullus 2	31	42	54	30	50	50
13	Abu Khashaba 1	31	34	0	30	40	28
14	Abu Khashaba 2	31	38	36	30	40	28
15	Abu Khashaba 3	31	43	49	30	39	52
16	Rosetta 1	31	31	15	30	28	35
17	Rosetta 2	31	37	4	30	28	35
18	Rosetta 3	31	42	35	30	28	54
19	Abu Qir 3	31	26	39	30	0	0
20	Eastern Harbor 1	31	12	33	29	54	10
21	Eastern Harbor 2	31	17	9	29	54	10
22	Eastern Harbor 3	31	22	58	29	54	10
23	El Mex 2	31	12	33	29	41	59
24	Sedi Kerir 1	31	2	26	29	30	25
25	El Hammam 1	30	53	15	28	59	57
26	El Hammam 2	30	59	59	29	0	15
27	Alameen 1	31	0	18	28	45	20
28	Alameen 2	31	4	17	28	45	20
29	El Dabaa 1	31	5	12	28	30	43
30	El Dabaa 3	31	9	48	28	30	24
31	Foka 1	31	16	51	27	59	57
32	Alm El Room 1	31	16	14	27	30	24
33	Marsa Matrouh 1	31	27	16	26	59	38
34	El Shalia 1	31	37	41	26	30	23
35	El Shalia 2	31	42	54	26	30	5
36	Sedi Barrani 1	31	40	26	25	59	56
37	Sedi Barrani 3	31	45	2	26	0	14
38	El Salloum 1	31	34	37	25	15	28
39	El Salloum 2	31	41	3	25	15	28

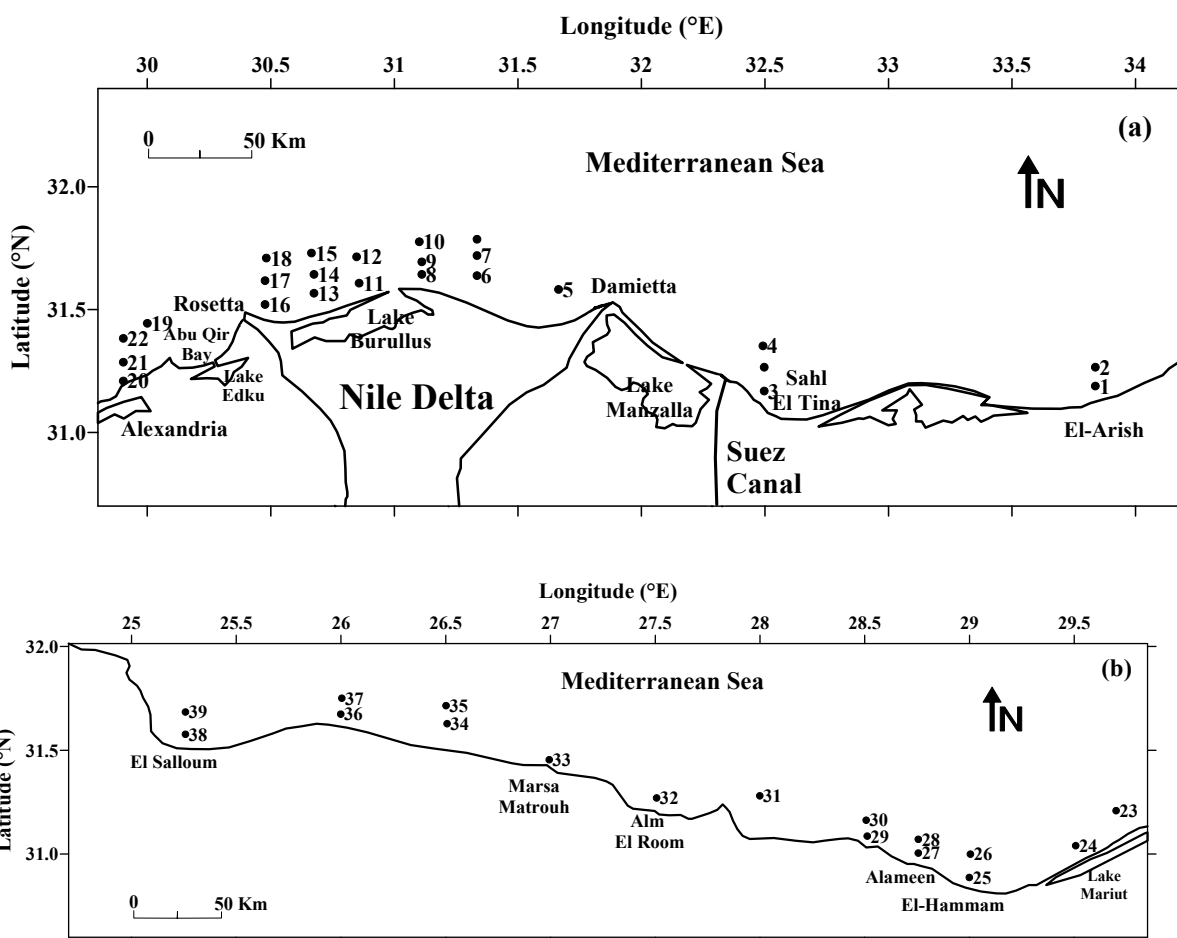


Figure 1: Distribution of sampling stations along the Egyptian Mediterranean Sea during 2008; a) eastern sector and (b) western sector.

The heavy-metal pollution levels in the collected sediments were measured using the Index of Geoaccumulation (I_{geo}) (Müller, 1987) which consists of six grades. The highest grade reflects 100-fold metal concentration relative to background values:

$$I_{geo} = \log_2 [C_n / (1.5 \times B_n)]$$

Where C_n is the measured concentration of element n in sediment sample, and B_n is the background concentration of element n . A factor of 1.5 is used because of possible variations in background data due to lithogenic effects (Müller, 1987).

Organotin compounds were determined according to Tsuda *et al.* (1987) as follows; ten grams of dry sediment was placed into 500 ml separating funnel and extracted with 50 ml hexane for 30 min after adding 50 ml water and 5 ml HCl. The mixture was centrifuged at 2500 rpm for 5 min, 30 ml of organic layer were transferred to 50 ml round-bottom flask. The organic layer was evaporated nearly to dryness (0.1 ml) in a vacuum at 40°C. The residue was dissolved in 1 ml ethanol. Then, 2 ml of the hydrogenation reagent (1 g of $NaBH_4$ dissolved in 40 ml ethanol) was added with shaking and left for standing for 10 min at room temperature. Five ml of water was added to the reaction mixture, shaken slightly, and transferred to 50 ml

separating funnel. The flask was rinsed with 5 ml portions of water, and transferred to the funnel then extracted for 5 min with 5 ml hexane after adding 5 g NaCl. Hexane was passed through silica gel column to elute butyltin hydrides. The first 20 ml was collected in a round-bottom flask, evaporated to about 2 ml under reduced pressure at 40°C. The concentrate was transferred into 5 ml gradual test tube, rinsing flask with hexane, and the volume was adjusted to 1 ml under gentle stream of pure nitrogen gas. The final extract was then injected into gas chromatography/electron capture detector, GC/ECD (HP 5890 II). The chromatographic column was HP-5 capillary column (30 m x 0.32 mm x 0.25 μ m); 5% diphenyl and 95% dimethyl polysiloxane, non-polar 60 to 325°C). N_2 was used as carrier gas with flow rate of 2 ml/min. The injection port and detector line were at 300 and 310°C, respectively. The column was programmed from 80°C for 3 min initial hold to 310°C for 8 min final hold at 5°C/min rate. Recoveries of dibutyltin and tributyltin from spiked samples varied from 85-102%. The detection limits of dibutyltin and tributyltin were 0.5 and 1.0 ng/g.

3. Results and Discussion

3.1. Total Tin

Tin has several applications, such as a protective coating, in solders, bearings and other alloys (Lide, 1991). Generally, Sn compounds are sparingly soluble in water and are likely to partition to soils and sediments. Commercially most organotin compounds used are relatively immobile in environment media due to their low vapor pressures, low water solubility and high affinity for soil and organic sediments (Blunden and Chapman 1984). Inorganic Sn can not be degraded in the environment, but may undergo oxidation-reduction, ligand exchange and precipitation reactions (HSDB, 2003). Degradation of organotin compounds in sediments is much slower than in water, and half lives have been estimated to be several years (Alzieu *et al.*, 1991).

In the present study, concentrations of total Sn ranged from 1.31 to 34.88 and from 7.68 to 61.30 $\mu\text{g/g}$; dry wt with average values of 8.91 and 42.12 $\mu\text{g/g}$; dry wt for the eastern and western sectors, respectively (Tables 2 and 3, Figures 2 and 3). However, the maximum concentration of 61.3 $\mu\text{g/g}$; dry wt was measured at El Hammam (station 26) of the western sector. This location is affected mainly by heavily oil processing and ships discharge, using organotin compounds as antifouling paints at SUMED (SUMED Company for oil). Moreover, the presence of a maximum concentration of 34.88 $\mu\text{g/g}$; dry wt at the eastern harbor (station 21) may be due to the fact that this harbor is one of the heaviest fishing activities in Alexandria. Taking into consideration the number of ships and the time spent in dry dock area, it can be concluded that the main source of Sn in the harbor could be the leaching from ships due to the use of tributyltin in dry docking on hulls of new vessels and on older vessels during dry docking.

This study reported that I_{geo} values for Sn ranged from -0.2 to 4.6 and from 2.4 to 5 for the eastern and western sector, respectively, which indicated unpolluted ($I_{\text{geo}} < 1$), very little polluted ($1 < I_{\text{geo}} < 2$), little polluted ($2 < I_{\text{geo}} < 3$), moderately polluted ($3 < I_{\text{geo}} < 4$), highly polluted ($4 < I_{\text{geo}} < 5$), and very highly polluted ($I_{\text{geo}} > 5$) (Ruiz *et al.*, 1998). These results showed that the quality of the sediment samples of the eastern sector varied between unpolluted to highly polluted while in the western sector, it varied from little polluted to highly polluted level. This could be attributed to different anthropogenic sources.

3.2. Organotin compounds

The major pathway of TBT entry into marine environment has been known through direct leaching from antifouling paints into water, and then adsorption and partitioning to suspended particulate matter with subsequent sedimentation to sediments (Díez *et al.*, 2005). In general, TBT compounds produced from

shipping may enter the environment in five ways: a) at the time of ship construction; (b) when vessels are stationary in port (static leaching); (c) when vessels are under way at sea (dynamic leaching); (d) when vessels are in dry dock for repairing and maintenance including repainting and (e) when vessels are scrapped.

Tables 2 and 3 show that tributyltin (TBT) concentrations in sediments varied widely depending on the location and they ranged from 0.15 to 4.35 and from <DL to 8.55 $\mu\text{g/g}$; dry wt with average values of 2.29 and 3.74 $\mu\text{g/g}$; dry wt for the eastern and western sectors; respectively. It is clear that the western sector exhibited higher concentration of TBT than that of the eastern one (Figures 4 and 5) which may be attributed to the petroleum activities especially, at Sedi Kerir and Alameen areas where two oil terminals are found. In addition to heavily transport and shipping activities of large vessels in the western sector where TBT was used as antifouling paints. The highest level of TBT was observed at El- Dabaa (8.55 $\mu\text{g/g}$; dry wt), while the lowest one was at Abu Qir (0.15 $\mu\text{g/g}$; dry wt). This finding in a good agreement with Lee *et al.* (2006) where the highest level of TBT was in sediments from Taiwanese harbors in an area where some oceanic vessels and larger commercial ships operate. Moreover, Tables 2 and 3 indicated that DBT is undetected at most stations, while TBT exhibited the highest concentrations reflecting recent input of TBT into the investigated area and consequently low TBT degradation. It is known that TBT degradation rate in sediments is slower than in water column, particularly in anaerobic conditions. The half life of TBT in sediments is in the range of years rather than days or weeks in water column as reported by Cima *et al.* (2003). Although abiotic degradation occurs, the process remains less important than biological action (WHO, 1990). Microbial degradation of TBT to either DBT or MBT takes a period of days or weeks in water, years in oxic sediments and more than that in anoxic sediments as mentioned by Dowson *et al.* (1993b). The degradation products have generally been assumed to be less toxic than TBT because they are less lipophilic. Furthermore, bacterial communities degrading TBT might be depend on salinity and other environmental factors (Pereira *et al.*, 1999).

Moreover, the extreme stability of TBT in the sedimentary compartment has been confirmed by high concentrations found in the deep sediments of several harbor areas (Alzieu *et al.*, 1991). Percentages of TBT ranged from 0.87 to 55.31% and from 0.17 to 18.39 % for eastern and western sectors, respectively. In addition, a significant correlation was found between TBT and total Sn ($r = 0.356$, $n = 39$, $P = 0.05$). This reflects the influence of historical anthropogenic pollution, fishing and shipping activities at this area.

The Australian sediment quality guidelines for TBT are 5 ng/g and 70 ng/g for low and high trigger values (ANZECC and ARMCANZ, 2000). Sediments taken from different areas of the present study contain

Table 2: Concentrations in $\mu\text{g/g}$; dry wt for different forms of Sn in sediment samples collected from the eastern sector during 2008.

St. No.	Sector		DBT	TBT	Sn
1	El-Arish	El-Arish 1*	ND	1.15	3.84
2		El-Arish 3	ND	3.59	8.51
Average			ND	2.37	6.18
3	Sahl El Tina	Sahl El Tina 1	0.73	3.48	9.41
4		Sahl El Tina 3***	5.38	0.84	4.31
Average			3.06	2.16	6.86
5	Damietta	Damietta 1	ND	3.04	2.89
6	Baltim	Baltim 1	2.16	2.14	4.13
7		Baltim 3	ND	1.39	13.34
Average			1.08	1.77	8.74
8	Gamasa	Gamasa 1	ND	2.75	3.32
9		Gamasa 2**	ND	2.83	4.57
10		Gamasa 3	0.25	2.45	8.92
Average			0.08	2.68	5.60
11	Burullus	Burullus 1	ND	2.24	5.06
12		Burullus 2	0.85	1.72	2.99
Average			0.43	1.98	4.03
13	Abu Khashaba	Abu Khashaba 1	0.45	3.57	3.55
14		Abu Khashaba 2	ND	0.20	9.40
15		Abu Khashaba 3	ND	2.46	12.13
Average			0.15	2.08	8.36
16	Rosetta	Rosetta 1	0.50	2.72	11.45
17		Rosetta 2	ND	2.71	16.13
18		Rosetta 3	ND	1.53	2.69
Average			0.17	2.32	10.09
19	Abu Qir	Abu Qir 3	ND	0.15	1.31
20	Eastern Harbor	Eastern Harbor 1	1.23	4.35	3.21
21		Eastern Harbor 2	ND	2.0	34.88
22		Eastern Harbor 3	1.11	2.85	29.89
Average			0.78	3.07	22.66
Total average			0.87	2.29	8.91
Minimum			ND	0.15	1.31
Maximum			2.16	4.35	34.88

* 10 m, ** 20 m, *** 30 m depth; ND = below detection limit.

Table 3: Concentrations in $\mu\text{g/g}$; dry wt for different forms of Sn in sediment samples collected from the western sector during 2008.

St. No.	Sector		DBT	TBT	Sn
23	El Mex	El Mex 2	ND	6.98	43.14
24	Sedi Kerir	Sedi Kerir 1*	1.13	6.69	40.17
25	El Hammam	El Hammam 1	ND	0.02	45.80
26		El Hammam 2**	ND	3.96	61.30
Average			ND	1.99	53.55
27	Alameen	Alameen 1	ND	0.18	44.47
28		Alameen 1	ND	3.01	47.29
Average			ND	1.59	45.88
29	El Dabaa	El Dabaa 1	ND	3.25	46.55
30		El Dabaa 3***	ND	8.55	44.04
Average			ND	5.90	45.30
31	Foka	Foka 1	ND	1.29	43.41
32	Alm El Room	Alm El Room 1	ND	3.46	7.68
33	Marsa Matrouh	Marsa Matrouh 1	1.29	5.66	46.28
34	El Shallia	El Shallia 1	ND	2.41	45.89
35		El Shallia 2	ND	ND	39.39
Average			ND	1.21	42.64
36	Sedi Barrani	Sedi Barrani 1	ND	2.30	14.15
37		Sedi Barrani 3	ND	5.82	46.61
Average			ND	4.06	30.38
38	El Salloum	El Salloum 1	ND	ND	52.77
39		El Salloum 2	ND	2.62	47.10
Average			ND	1.31	49.94
Total average			1.21	3.74	42.12
Minimum			ND	ND	7.68
Maximum			1.29	8.55	61.30

*30 m, **50 m, ***100 m depth; ND = below detection limit

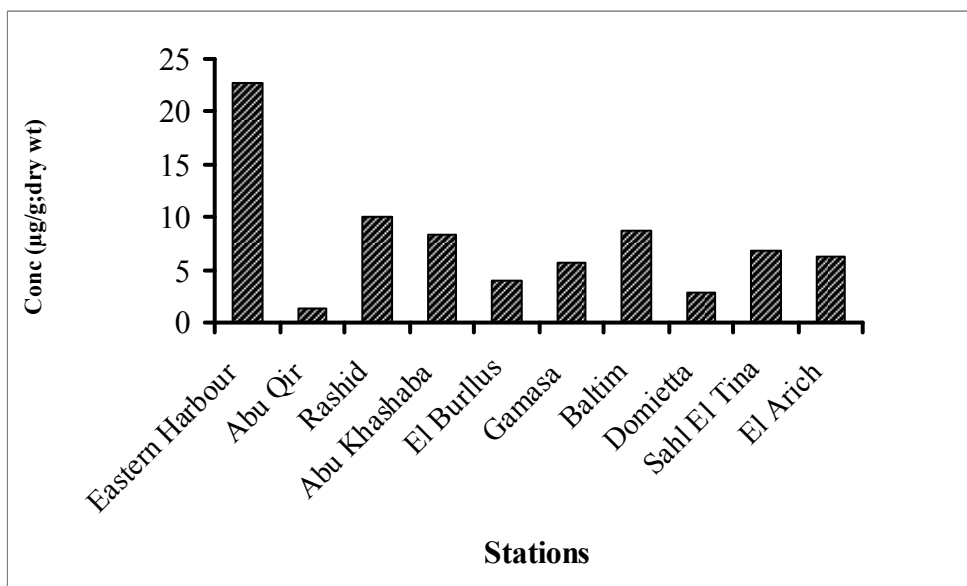


Figure 2: Distribution of total tin concentration (µg/g; dry wt) in sediment samples collected from the eastern sector of the Egyptian Mediterranean Seacoast during 2008.

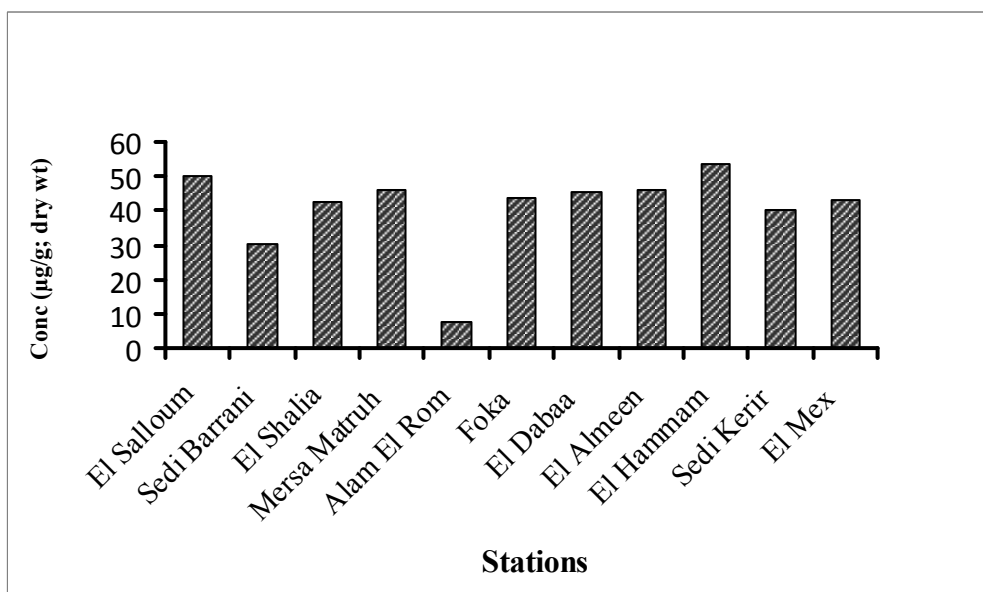


Figure 3: Distribution of total tin concentration (µg/g; dry wt) in sediment samples collected from the western sector of the Egyptian Mediterranean Sea coast during 2008.

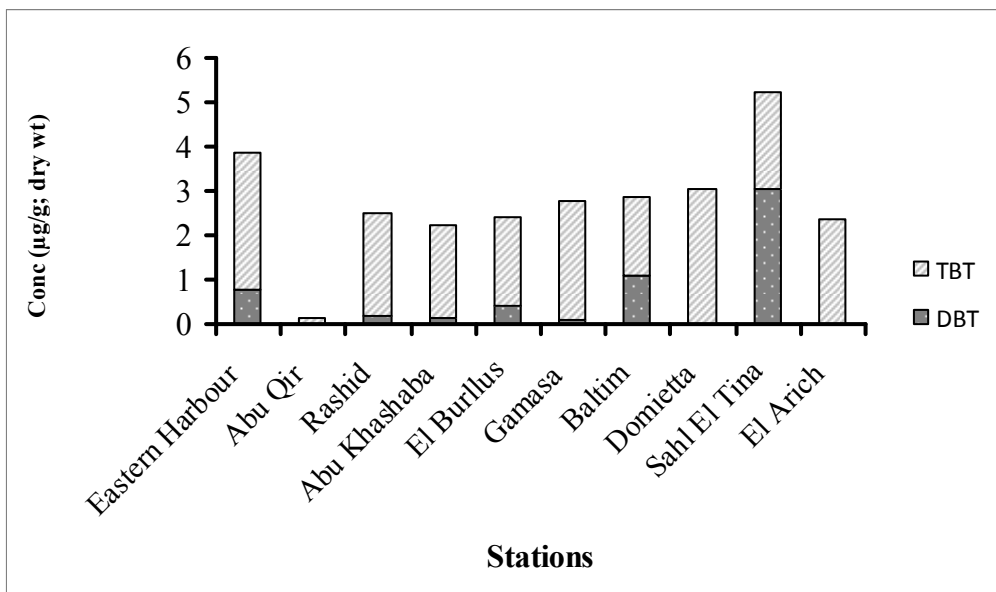


Figure 4: Distribution of DBT and TBT compounds ($\mu\text{g/g}$) in sediment samples collected from the eastern sector along the Egyptian Mediterranean Sea coast during 2008.

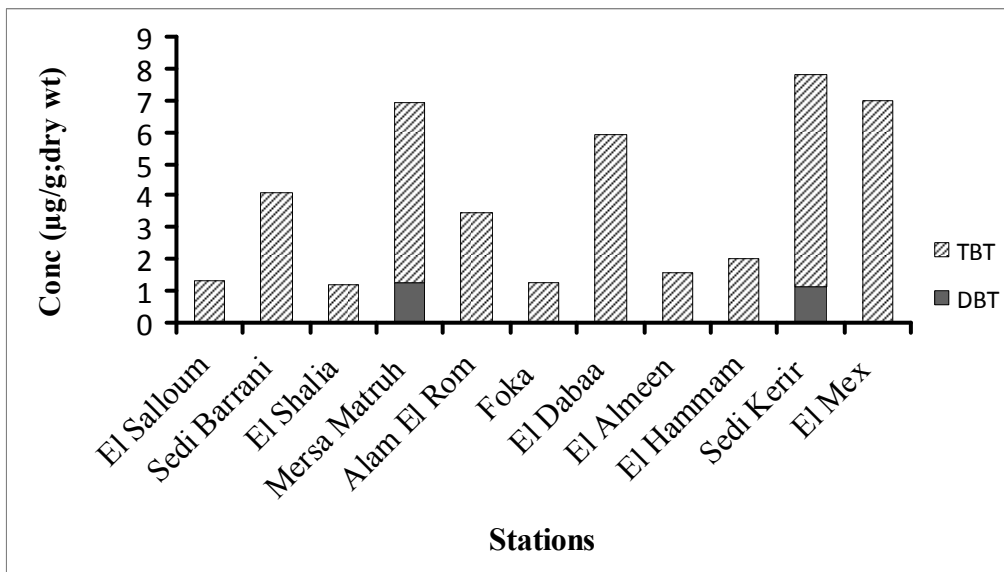


Figure 5: Distribution of DBT and TBT compounds ($\mu\text{g/g}$) in sediment samples collected from the western sector along the Egyptian Mediterranean Sea coast during 2008.

TBT concentrations higher than the highest trigger value, suggesting that these sediments may pose a threat to a benthic biota. Thus, high levels of TBT in sediment samples suggested its widespread contamination and could be indicative of the continuing usage of TBT-based antifouling paints on ship hulls.

Dowson *et al.* (1993a) introduced a classification for TBT concentration in sediments, characterizing levels below 3 ng/g as uncontaminated, 3-20 ng/g as light contaminated, 20-100 ng/g as moderately contaminated, 100-500 ng/g as highly contaminated and above 500 ng/g as grossly contaminated. Comparing our results with this scheme, sediments of the Egyptian Mediterranean coasts is highly to grossly contaminate.

In addition, sediment samples in the present study contain TBT concentrations (ND-8.55 µg/g dry wt) higher than most of the developed and developing countries such as USA (0.0007-0.009 µg/g dry wt, Pereira *et al.*, 1999) and Malaysia (0.002-1.100 µg/g dry wt, Sudaryanto *et al.*, 2004). They were comparable with that measured in Taiwanese coast (ND- 8.5 µg/g dry wt, Lee *et al.*, 2006). However, sediments from Spanish north-eastern and south-eastern coast (0.124-18.722 µg/g dry wt, Diez *et al.*, 2002), Greek Attica peninsula (0.610- 24.400 µg/g dry wt, Tselentis *et al.*, 1999), German North Sea and Baltic Sea marinas (0.073-15.130 µg/g dry wt, Biselli *et al.*, 2000), Sanricu coast, Japan (0.002-14 µg Sn/g dry wt, Harino *et al.*, 2007) showed higher TBT levels than those of our record.

4. Conclusions

The distribution of TBT and DBT in sediments of the Egyptian Mediterranean coast was investigated in the present study. The obtained results revealed a wide variation in TBT distribution depending on the locations and shipping activities. TBT was the predominant species with average values of 2.29 and 3.74 µg/g dry wt for the eastern and western sectors, respectively. The western sector exhibited higher values of TBT concentrations than those of the eastern one. This could be attributed to the shipment activities in addition to the presence of Sedi Kerir power station. A significant positive correlation ($r = 0.36$, $P \leq 0.05$) was found between TBT and total tin (ΣSn), implying considerable anthropogenic input of butyltin compounds to total tin contamination levels. Sediments at different stations of the present study contained higher TBT concentrations than the highest trigger value (70 ng/g), suggesting a threat to benthic biota of the region. In spite of the banning or regulation of using TBT in some countries, contamination continues in the aquatic environment, and environmental concentrations remain high enough to warrant continued concern. So serious actions must be taken to

restrict and regulate the use of organotin compounds as antifouling paints by the Egyptian port authorities.

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مركبات القصدير العضوية في رسوبيات البحر الأبيض المتوسط المصرية - مصر

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تمت دراسة مركبات القصدير العضوية في رسوبيات سواحل البحر المتوسط المصرية ممثلة في 39 محطة خلال صيف 2008. تم استخدام جهاز كروماتوجرافيا الغاز في تحليل تلك المركبات بمنطقة الدراسة. بالإضافة الى استخدام جهاز الامتصاص الذرى (وحدة الجرافيت) في قياس محتوى القصدير الكلى و استخدامها في حساب نسب المركبات العضوية بالعينات المجمعة. تم رصد تركيزات عالية من مركب ثلاثى بيوتيل القصدير (TBT) وكان متوسط التركيزات 2.29 و 3.74 ميكرو جرام / جرام لمناطق الشرق و الغرب على التوالي. بينما لم تسجل مركبات ثنائى بيوتيل القصدير بشكل واضح فى معظم المحطات . كما وجدت علاقة بين مركبات TBT و القصدير الكلى مما يدل على أن استخدام TBT فى الأنشطة البشرية قد أسهم فى زيادة المحتوى الكلى للقصدير. تخطت تركيزات TBT الحد المؤثر و هو 70 نانو جرام/ جرام . و طبقا لتركيزات TBT يمكن تصنيف رسوبيات البحر المتوسط أنها عالية إلى شديدة التلوث بهذه المركبات.