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## Levels of tin in core sediments along the Alexandria Coast, Egypt

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Tin concentrations were determined in surface and core sediments from three hot spots along the Alexandria coast, namely: Abu-Qir Bay, Eastern Harbour, and Western Harbour. The mean concentrations in surface sediment were 2.434, 3.212, and  $5.572 \,\mu g/g$  dry weight for Abu-Qir Bay, Eastern Harbour, and Western Harbour, respectively. A sharp decrease in tin level in core sediments with depth was observed in almost all locations except for core 4 in Abu-Qir Bay and core 17 in the Eastern Harbour, where the sub-sample at the 5 cm level recorded the highest tin concentrations.

Keywords: Tin; Sediment; Core sediment; Eastern Harbour; Western Harbour; Abu-Qir Bay; Egypt

#### 1. Introduction

In nature, Sn occurs predominantly as the mineral cassiterite  $(SnO_2)$  and has an average crustal abundance of  $3 \text{ mg kg}^{-1}$  [1]. Tin was one of the first metals used by mankind and is still widely used today. Implements made from Sn date back as far as 300 BC [2]. Starting with the Industrial Revolution, inorganic tin compounds were produced for various purposes as a protective coating for steel, bearings, and other alloys. Around 1940, the industrial production of organotin compounds started as a consequence of their use as stabilizers in polyvinyl chloride, homogeneous catalysts for vulcanization, and biocidic agents [3]. The biocidal preparations include agrochemicals, mainly fungicides, used for the control of fungus. They are also used as preservatives of wood and cellulose compounds such as cotton textiles and cellulose-based household filters. Triorganotin compounds are used as bactericidal disinfectants. One major use is as an antifouling agent in marine paints [4, 5]. Tin, like other metals discharged into estuarine and coastal marine waters, is usually adsorbed onto particle surfaces and incorporated into sediments [6]. Hence, the sediments represent an important source of contamination to both the overlying water column and benthic organisms with undoubtedly ecotoxicological implications [7]. To evaluate the quality of the aquatic systems, trace elements can be determined in water samples, sediment samples, or aquatic organisms. Analysis of the sediment

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samples presents several advantages such as the highest concentration of trace elements or providing information about the changes in concentration levels over time [8, 9]. Because the crustal abundance of Sn is relatively low and because Sn is used in many industrial manufacturing processes, Sn is a potentially important indicator of anthropogenic contamination [10]. Therefore, the present work was planned in order to determine the concentration of total tin in surface sediments and to determine the relationships of tin with the depth of several core sediments in three main contaminated areas along Alexandria coast.

#### 2. Materials and methods

The areas of study comprise three docking areas in the Alexandria region. These areas are the Western Harbour, the Eastern Harbour, and Abu-Qir Bay (figure 1). Each of these areas has distinct characteristics from the others, as they serve different purposes. Alexandria Western port is the largest commercial port in Egypt, and about 70% of Egypt's foreign trade is served at this port. Exporting and importing activities of raw materials, general goods, fertilizers, cement, wood, coal, oil molasses, and petroleum are served at this port beside the location of the Egyptian Maritime Passengers Port inside it. Different types of ships, carriers, submarines, containers, tug boots, and floating docks use this port for different purposes. On the other hand,



Figure 1. Map of sample locations.

Station	Site no.	Latitude	Longitude	Water-column depth (m)	Core-sediment depth (cm)	Position description
Abu-Qir Bay	1	31° 16′ 35.4″ E	30° 10′ 37.3″ N	5.5	_	Outside port
	2	31° 19′ 26.8″ E	30° 04′ 52.1″ N	11.0	_	Vessel anchorage area, inside port
	3	31° 19' 04.0" E	30° 04′ 28.8″ N	8.8	30.0	In front of Teamsah port
	4	31° 19′ 81.1″ E	30° 04′ 35.0″ N	10.5	28.0	Traffic pathway inside port
	5	31° 16′ 24.4″ E	30° 09′ 27.8″ N	7.5	18.0	In front of Petrojet port
Western Harbour	6	31° 09′ 49.5″ E	29° 50′ 25.5″ N	13.0	22.5	Anchorage area, outside port
	7	31° 10′ 26.7″ E	30° 52′ 12.9″ N	6.3	12.0	In front of Alexandria Shipyard, Dry dock (old dock)
	8	31° 16′ 75.0″ E	29° 84′ 41.0″ N	7.0	-	In front of Alexandria Shipyard, Dry dock (new dock)
	9	31° 11′ 05.7″ E	29° 52′ 27.3″ N	9.3	-	In front of coal quay
	10	31° 11′ 26.4″ E	29° 52′ 21.2″ N	13.5	27.0	Traffic pathway inside port
	11	31° 11′ 38.3″ E	29° 52′ 39.7″ N	10.3	24.0	In front of passengers station port
	12	31° 11′ 51.7″ E	29° 52′ 25.0″ N	10.0	-	In front of Egyptian shipbuilding and repair company
	13	31° 11′ 54.2″ E	29° 52′ 48.1″ N	4.5	12.0	Infront of Alexandria Drydock and slipway
Eastern Harbour	14	31° 10′ 33.5″ E	29° 49′ 26.2″ N	17.0	18.0	Vessels anchorage, outside port
	15	31° 12′ 53.2″ E	29° 54′ 12.5″ N	9.0	18.0	Entrance of Eastern Port, Bogas
	16	31° 12′ 40.9″ E	29° 53′ 08.2″ N	4.0	16.0	Inside Eastern Port, fishing boats area
	17	31° 12′ 37.5″ E	29° 53′ 01.5″ N	3.0	18.5	In front of private slipway, El-Sakala

Table 1. Locations of samples from Abu-Qir Bay, Western Harbour, and Eastern Harbour.

Step no.	Temperature (°C)	Time (s)	Gas flow (1 min <sup>-1</sup> )	Read command
1	85	5	3	No
2	95	30	3	No
3	120	10	3	No
4	700	10	3	No
5	700	5	3	No
6	700	2	0	No
7	2600	1	0	Yes
8	2600	2	0	Yes
9	2700	3	3	No
10	60	13.2	3	No

Table 2. Furnace parameters.

the Eastern Harbour and Abu-Qir Bay are mainly fishing ports. In the Eastern Port, there are many small private ship yards (slipways) used for building and maintenance of fishing boats, yachts, and fun small boats. There are two canals discharging freshwater directly inside the Western Harbour as well as a mixture of agricultural, industrial, and domestic sewage waste water into El-Mex Bay [11]. The Eastern Harbour receives a considerable amount of sewage discharge [12], while Abu-Qir Bay receives various types of discharges (industrial, agricultural, and sewage wastes) [13].

Sediment core samples were collected from 17 stations to cover the three areas of study (figure 1) by means of a simple gravity corer from depths ranging from 5 to 25 m as shown in table 1. The core samples were sub-sampled at 5 cm intervals and refrigerated until analysis. The sub-samples were analysed for their water content, total organic carbon, carbonate content, and particle size according to Folk [14]. Total tin in core sediment samples was determined according to the method described by UNEP/EIAEA [15]. An exact weight of dry sample (about 0.2 g) was placed in a Teflon vessel, and 10 ml of concentrated  $HNO_3/HClO_4/HF$ mixture (4:1:6) was added to each sample. After complete digestion, the sample was evaporated to dryness; the temperature was then increased gradually to 120 °C. The sample was cooled to room temperature and rinsed with 5 ml of 1% HNO<sub>3</sub>, and then the residue was transferred to a 25 ml measuring flask. The quantitative determination of total tin in sediment samples was carried out using a flameless Varian 10 Plus atomic absorption spectrophotometer. A high-intensity tin hollow cathode lamp (7 mA) at 235.5 nm resonance and 0.5 slit width was used. The optimum temperature, optimum acetylene gas flow, and times for drying, ashing, and atomization steps to obtain efficient pyrolysis and atomization are listed in table 2. For the preparation of a standard solution, 1 g of tin metal was dissolved in 100 ml of hydrochloric acid, warmed to  $60^{\circ}$ , cooled, and diluted to 1 l to give  $1000 \,\mu g/ml$  of Sn in 1:9 HCl. A

Sample no.	Concentration $(\mu g g^{-1})$	Certificate value	CVa
Sumple no.	(#55)	Varue	
1	2.5		
2	2.37		
3	2.37		
4	2.37		3.61
5	2.25		
6	2.35		
Mean $\pm$ S.D.			

Table 3. Replicate analysis for IAEA/Run SD-2/TM.

<sup>a</sup>95% confidence interval for reference material certificate value.

series of standard solutions (10, 20, 30, 40, and 60 ng/ml) were prepared to make the standard curve, and no chemical modifier was added. The whole analytical procedure for sediment was validated by analysing a standard reference material (IAEA/Run SD-2/TM) (table 3).

#### 3. Results and discussion

The water content, total organic carbon (TOC %), calcium carbonate, and grain size analysis in the surface and core sediment samples are listed in table 4.

Water content reflects the ability of the sediment to hold water molecules between its particles, which is mainly a function of particle size and mineral composition. It affects also the rate of reactions particular, the reduction oxidation reaction, and pH. The highest water content was recorded in Abu-Qir Bay (38.37%), while the lowest value was obtained in the Eastern Harbour (21.82%). The water content in the three studied areas is closely related to the particle size of sediment, where it is negatively correlated with the sand fraction (r = -0.748, p = 0.000) and positively correlated to the silt fraction (r = 0.739, p = 0.000).

TOC in the sediments reflects the high productivity of the water column that contributes organic detritus to bottom sediments and reflects the terrestrial input from land-based sources. The distribution pattern of TOC in the three areas was different, as shown in table 4. In Abu-Qir Bay, the TOC in surface sediment fluctuated between 1.38% at station 5 and 7.06% at station 4 with an average value of 3.28%. In the core sediment, the TOC pattern decreased from the surface layer to 5 cm depth, then increased from 5 cm to 10 cm depth, and remained nearly constant at 20 cm depth (figure 2). The high values at stations 3 and 4 reflect the influence of the pulp paper and food industries around the bay since most of these companies dump their wastes into the bay. The TOC of Western Harbour sediment ranged from 1.70 at station 8 to 8.72 at station 13 with an average value 3.97%. The high TOC was recorded at depth 5-6 cm in almost all core sediments in the Western Harbour as shown in figure 3. The relatively high values recorded at station 7 in front of the Alexandria Shipyard and station 13 in the Alexandria Port dry dockyard and slipway as shown in table 4 reflect the effect of dumping into the sea material used from cleaning operations. The sediment of TOC in the Eastern Harbour records a relatively average value (2.24%) compared with that recorded in the Western Harbour and Abu-Qir Bay. Station 15 outside the Port showed the lowest value in the Eastern Harbour as shown in table 4. The TOC% is weakly correlated with particle size for both sediment sand% and silt%.

Tin forms simple compounds with oxides, halides, sulfates, phosphates, and carbonates in the oxidation states (+2) and (+4). Tin(II) species are readily oxidized to Sn(IV) species by relatively mild conditions such as dissolved atmospheric oxygen. The rate of oxidation of Sn(II) can be reduced, particulary in solutions which contain sufficiently strong electron species such as fluorides and chlorides. In solutions above pH 6, oxidation is more rapid, and Sn(II) compounds can function as relatively strong reducing agents [16].

The concentrations of Sn in the fine fraction ( $<63 \,\mu$ m) of surface and core sediments are shown in table 5. All the data (in  $\mu$ g/g), averaged for three independent samples, were calculated based on dry matter. The average concentration of total tin in surfacial sediments fluctuated from  $5.572 \,\mu$ g/g in the Eastern Harbour to  $3.212 \,\mu$ g/g in the Western Harbour, to  $2.430 \,\mu$ g/g in Abu-Qir Bay.

Station 2 (Anchorage area) in Abu-Qir Bay showed the highest tin content reflecting the activities carried out in this area, followed by station 4 ( $2.65 \mu g/g$ ), which is attributed to the traffic pathway inside the port, while station 5 (in front of Petrojet Port) showed the lowest value (figure 4). The total amount of tin in the core sediment samples collected from Abu-Qir

Table 4.	Water content, TOC, carbonate content, and grain-size analysis for surface and core sediments of the
	study area.

Station number	Core length	Water content (%)	TOC (%)	CaCO3 (%)	Sand (%)	Silt (%)	Texture class
1	Surface	21.63	2.37	11.78	85.57	14.43	v.f. sand
2	Surface	24.22	1.61	12.5	78.59	21.41	f. sand
3	Surface	50.96	3.96	32.42	19.75	80.25	c. silt
	5–6 cm	50.02	4.17	27.16	18.62	81.38	c. silt
	10–11 cm	52.11	4.51	38.26	16.92	83.08	c. silt
	15–16 cm	50.98	3.88	14.42	12.5	87.5	c. silt
	20–21 cm	52.2	3.76	28.33			
	25–26 cm	43.66	3.69	25.15			
4	Surface	44.48	7.06	32.56	67.89	23.11	v.f. sand
	5–6 cm	61.79	4.53	32.44	61.03	38.97	v.f. sand
	10–11 cm	43.95	3.59	65	69.68	30.32	v.f. sand
	15–16 cm	35.55	3.48	17.6	67.78	32.22	v.f. sand
	20–21 cm	30.53	3.47	6.12	99.5	0.5	f. sand
	25–26 cm	21.37	1.58	8.92	96.67	3.33	f. sand
5	Surface	22.96	1.38	12.79	82.22	17.78	v.f. sand
	5–6 cm	21.63	1.37	11.78	85.57	14.43	v.f. sand
	10–11 cm	24.22	1.61	12.92	78.59	21.41	v.f. sand
6	Surface	31.43	1.85	66.13	94.04	5.96	f. sand
	5–6 cm	31.75	1.37	69.02	96.16	3.84	f. sand
	10–11 cm	39.38	1.88	84.16	97.46	2.54	f. sand
	15–16 cm	38.1	1.77	95.39	96.15	3.85	f. sand
	20–21 cm	33.29	1.86	89.82	98.25	1.75	m. sand
7	Surface	38.1	6.6	67.81	84.55	15.75	f. sand
	5–6 cm		5.98	69.84	77.5	22.5	v.f. sand
	10–11 cm		7.47	69.39	73	27	v.f. sand
8	Surface	18.93	1.7	91.06	100	0	v.f. sand
9	Surface	20.15	3.37	86.85	92.91	7.09	v.f. sand
10	Surface	20.15	3.37	86.85	92.91	7.09	c. sand
	5–6 cm		4.08	71.07	14.82	85.18	c. silt
	10–11 cm		4.08	34.86	0	100	c. silt
	15–16 cm		4.21	26.3	0	100	c. silt
	20–21 cm		4.81	45.71	10	90	c. silt
	25–26 cm		3.81	84.37	0	100	c. silt
11	Surface	33.29	4.44	37.25	44.79	55.21	v.f. sand
	5–6 cm		4.43	33.51	57.24	42.76	f. sand
	10–11 cm		5.22	61.27			
	15–16 cm		2.75	58.86			
10	20–21 cm	26.24	3.66	69.86	00	10	
12	Surface	26.34	1.76	12.66	90	10	
13	Surface	20.2	8.72	74.88			
	5–6 cm		6.86	70.41			
	10–11 cm	12.02	8.85	85.26	100	0	,
14	Surface	13.93	1.46	41.62	100	0	c. sand
	5-6 cm	15.41	1.88	31.18	100	0	c. sand
	10–11 cm	13.56	2.69		100	0	c. sand
1.5	15–16 cm	11.1	2	02.10	100	0	c. sand
15	Surface	12.27	1.8/	93.19	100	0	v.f. sand
	5-6 cm	16.25	1.85	92.29	100	0	v.r. sand
	10–11 cm	18.93	1.7	91.06	100	0	v.r. sand
16	15–16 cm	20.15	1./4	97.23	100	0	c. sand
10	Surface	23.49	2.32	91.4	90.55	3.43 5.77	m.sand
	5-0 cm	27.95	1.98	91.53	94.23	5.//	m.sand
17	10–11 cm	25.73	2.24	88.7	96.63	3.37	c. sand
1/	Surface	37.58	2.55	22.39	85.56	14.44	I. sand
	5-6 cm	20.34	1.76	12.66	90	10	I. sand
	10–11 cm	19.74	1.12		80.5	13.5	I. sand
	15–16 cm	12.26			89.45	10.55	m. sand

*Note*: v = very; m = medium; c = coarse; f = fine.



Figure 2. Variation of TOC% with depth core Abu-Qir Bay sediments.

Bay is shown in figure 5. It is evident that the surface layer of the sediment recorded the highest tin content and decreases towards the core depth except for the core of station 4, where the sub-sample at 5 cm showed the highest concentration. Based on the sedimentation rate of 22 cm per 100 yr, this layer corresponds to the year 1975 [17]. This is attributed to the first introduction of TBT in this area, associated with large military and commercial ships.

The distribution of total surficial sediment in the Western Harbour showed that station 8 (in front of the Alexandria shipyards dry dock) recorded the highest value (7.44  $\mu$ g/g dw) followed by station 13 (in front of the Alexandria port dry dock and slipway) (5.63  $\mu$ g/g dw), reflecting the high activities of ships inside the ports. Stations 7 and 11 recorded relatively high values (figure 4), located in front of the Alexandria shipyard dry dock (old dock) and in front of the passenger station port, respectively, while station 6 outside the Eastern Harbour recorded the lowest value. The total tin concentration in core sediment decreases towards the depth in all studied stations in the Western harbour as shown in figure 5.

The highest value of total surfacial tin in the Eastern Harbour was recorded at station 17  $(10.16 \,\mu g/g \, dw)$  in front of the private slipway (El-Sakala) which is attributed to the ship activities in this area. Stations 15 and 16, located at the entrance of the Eastern Habour and inside it, respectively, showed approximately the same Sn concentration while station 14



Figure 3. Variation of TOC% with depth core Western Harbour sediments.

Location	Station no.	Surface	5–6 cm	10–11 cm	15–16 cm	20–21 cm	25–26 cm
Abu- Qir	1	1.86	_	_	_	_	_
Bay	2	5.36	_	_	_	_	_
5	3	1.52	0.52	0.11	0.104	nd	nd
	4	2.65	3.14	1.75	1.22	0.67	0.24
	5	0.78	0.17	nd	nd	_	-
Western	6	0.76	0.16	nd	nd	nd	_
Harbour	7	3.68	0.43	nd	_	_	_
	8	7.44	_	_	_	_	_
	9	1.78	_	_	_	_	_
	10	0.92	nd	nd	nd	nd	_
	11	3.8	0.54	0.28	nd	nd	_
	12	1.69	_	_	_	_	_
	13	5.63	2.27	0.64	-	_	-
Eastern	14	3.28	0.26	nd	nd	_	_
Harbour	15	4.21	0.67	0.17	nd	_	_
	16	4.64	0.63	nd	_	_	_
	17	10.16	7.5	nd	nd	-	-

Table 5. Total tin concentration ( $\mu g g^{-1}$  dry wt.) in core sediments collected from Abu-Qir Bay, Western Harbour, and Eastern Harbour.

Note: nd: not detected.



Figure 4. Concentration of tin in surface sediment in Abu-Qir Bay, Western Harbour, and Eastern Harbour.

(outside the port ships anchorage area) recorded the lowest value. As shown in figure 5, the concentration of tin decreased with depth in most studied samples.

The sharp decrease in tin levels in the Eastern Harbour and Western Harbour core sediments was most noticeable at 5–6 cm, (25–30 yr) which reflects that tin contamination at the studied areas started after maritime installations. Like core 13 collected in front of the Alexandria dry dock and slipway, core 11 in front of the passenger station, and core 7 in front of the Alexandria shipyard, dry dock (old dock) in the Western Harbour, and core 17 collected in front of the private slipway (El-Sakala) in the Eastern Harbour.

The average concentration of total tin in surfacial sediment along the Alexandria coast in the present study ( $3.538 \pm 2.56$ ) is lower than that reported by Barciela-Alonso *et al.* [18] from Ria de Arousa (north-west of Spain) ( $5.0-20.8 \,\mu$ g/g dw) and very low compared with that found in Gipuzkoa, Spain ( $11-113 \,\mu$ g/g dw) [7], but higher than that reported by Aboul-Dahab [19].



Figure 5. Distribution of total tin in the core sediment in Abu-Qir Bay, Western Harbour, and Eastern Harbour.

#### 4. Conclusion

The highest concentration of surfacial sediment was recorded at station 17 in the Eastern Harbour in front of the private slipway, followed by station 8 in the Western Harbour, in front of Alexandria shipyard. The present study reveals that the surface layer of the sediment recorded the highest tin content and decreased towards the core depth except for the core for station 4 and 17 in Abu Qir and the Eastern Harbour, where the sub-sample at 5 cm showed the highest concentration, attributed to the first introduction of TBT in this area (associated with large military and commercial ships).

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