

## TRIBUTYLTIN CONTAMINATION IN SURFACE WATERS OF THE ALEXANDRIA COASTAL REGION

BY

LAILA ABD EL-FATTAH MOHAMED

Key words: Tributyltin, occurrence, seawater, Alexandria

### ABSTRACT

*Tributyltin (TBT) concentrations were determined in surfaces water of the Alexandria coast. Three hot spot sites namely, Western Harbor, Eastern Harbor and Abu Qir Bay were selected. The water samples were collected in summer 2000. The values of TBT in surface seawater samples ranged from 40 to 579 ng TBT/ L. The origin of TBT is in its use as antifouling agent in marine paints. These TBT concentrations are high and acute toxic effect on coastal organisms due to TBT may be expected in those sites.*

### INTRODUCTION

Tributyltin (TBT), the most butylin, can enter the marine environment through its use in antifouling paints and its other industrial applications (Snoij *et al*, 1987). Tributyltin effectively inhibits the growth of fouling organisms that attach to boat hulls, but also exhibits toxicity towards many non-target organisms. Tributyltin causes detrimental effects in Oyster spats and mussel larvae at water concentrations of ~50 ng TBT/ L (Hall and Pinkney, 1985; Lapota *et al*, 1993).

Concern over the ecotoxicological impacts of TBT led to regulations on the use of TBT based antifouling paint have been introduced by several countries (e.g. France, UK, USA and Japan) since the late 1980s (Champ and Wade, 1996). In many locations where regulation have been enforced, major improvements in water quality have been observed as tributyltin pollution has decreased in seawater and surface sediment (O'conner, 1996; US Navy and US EPA, 1997; Fent, 1996; Thomas *et al*, 2001; Michel *et al*, 2001).

Despite these improvements, some factors still limit a full recovery of heavily contaminated area, such as the long term persistence of TBT from hulls of large vessels, and more importantly, the lack of control measure in many developing countries (Stewart, 1996; Dowsen *et al.*, 1993). The main concern of environmental marine chemists and toxicologists is now the widespread distribution of butyltin compounds at low concentrations in many deep coastal water and organisms (Takahashi *et al.*, 1997; Michal and Averty, 1999).

Although, the studies have been conducted on the speciation of tin compounds in surface and core sediments of the Alexandria coastal belt by Abual-Dahab (1988; 1990), there still exists a general lack of information on the level of TBT in seawater and sediments; the source and fate of TBT, and the effect of TBT on local organisms inhabiting the coastal water of Alexandria.

The present study provides data on the level of TBT in surface seawater in relatively less reported area.

### **MATERIALS AND METHODS**

Fourteen surface water samples were collected at depth 3-17 m in summer, 2000 from three principal sites namely, Western Harbor (WH), Eastern Harbor (EH) and Abu Qir Bay (Fig. 1). The locations in this study encompassing the influence of commercial and navel vessels and repair facilities, fishing boat and also leisure vessels where, the source term for TBT entering the waters would be higher.

TBT determinations were carried out according to method described in Sherman and Carlson (1980). Briefly, seawater samples were extracted twice with hexane (20 ml). The extracts are then added to 1 ml  $H_2SO_4$  and the hexane slowly evaporated under reflux conditions when  $H_2SO_4$  reflux initiates, 5 drops of 30%  $H_2O_2$  was added drop wise to destroy the organic material and oxidize the tin. Heating continuous until the colorless refluxing acid reached to (ca. 10 ml), diluted solution of acetyl trimethylammoniumbromide (2.2 ml) was added and pH adjusted with NaOH (50%, ww), 1 ml of 2, 6, 7-trihydroxy-9-phenylisoxanthane-3-one (phenyl fluoresce) was added and the total volume adjusted to 25 ml with distilled water previously adjusted to pH 1.2 with  $H_2SO_4$ . Wait for 40 min at room temperature and measure the samples at wavelength 535 nm using 1 cm cell.

TRIBUTYL TIN CONTAMINATION IN SURFACE WATERS OF THE ALEXANDRIA

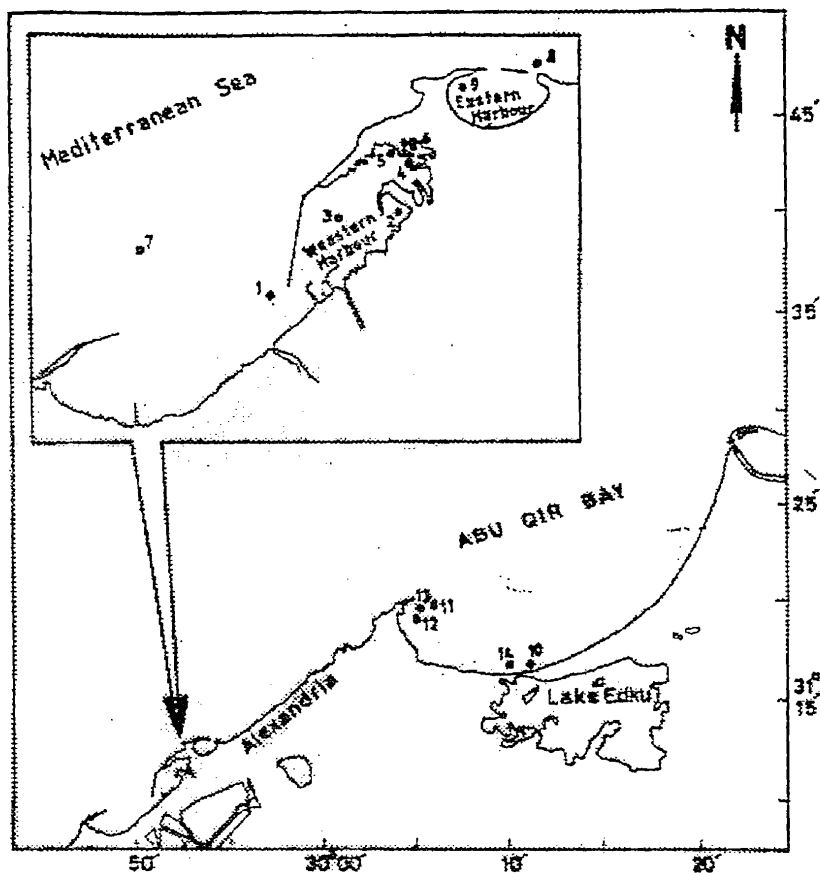


Fig. (1): Areas studied and sampling stations

For preparation of standard curve; 1, 2, 3 ml of standard solution contain  $1 \mu\text{g}$  TBT/ml into 250 ml separating funnel contain 200 ml of distilled water and extracted with hexane in the same manner as far sample.

The repeatability of measurements, as tested a six replicates, was  $\pm 15\%$  for seawater spiked with  $0.10 \mu\text{g}$  TBT/L.

The quantities of antifouling paints used in Alexandria docks and slipway during 1995-1999 are shown in Table (1).

Table 1: Antifouling paints quantities used (litèr) in Alexandria docks and slipway (1995-1999) (MRCC, 1995; 1999; 2000).

Location Name	1995	1996	1997	1998	1999
Alexandria Shipyard Company	10600	10850	9950	7900	8800
Egyptian Shipbuilding and Repair Company	12450	12150	12500	12310	12300
Alexandria Port Authority (Dock & Slipway)	1760	1480	1590	1650	1690
Egyptian Navy (Deck & Slipway)	1860	2450	3650	4160	4940
Private Ship Repair Company	1750	2200	2100	2300	2600

### RESULTS AND DISCUSSION

Results on the concentrations of TBT in Alexandria coastal water are shown in Table (2). Stations 1-6 located in WH (the major Egyptian commercial harbor) were subject to the influence of coastal source of TBT contamination concentrations between 92 and 597 ng TBT/ L. The highest TBT concentration with 597 ng TBT/ L was found to anchorage area, out side the WH. At stations 7-9 in EH (small fishing boat) TBT concentrations ranged from 46 ng TBT/ L to 459 ng TBT/ L. The greatest concentration, 459 ng TBT/ L, was found close to El-Bogaz, entrance of the Harbor.

These measurements indicates that contamination does not originated inside the EH but it is mostly transported into EH through El-Bogaz.

Surface water samples collected from stations 10-14 at Abu Qir Bay (ecologically important bay) show the most of the water have a relatively low TBT concentration 40 ng TBT/L, inside Bay, while the highest concentration, 579 ng TBT/L, was encountered at station 12 in front of Temssah Shipyard Company.

*TRIBUTYL TIN CONTAMINATION IN SURFACE WATERS OF THE ALEXANDRIA*

Table (2): Levels of TBT (ng TBT/ L) in the surface water samples collected from the area of study.

Site	N <sup>o</sup> Station	Position Description	Water Column depth (m)	Concentration of TBT (ng TBT/L)
Western Harbor	1	Anchorage area, Outside port	13.50	567
	2	In front of Alex. Shipyard, drydock	6.25	129
	3	Traffic pathway inside port	13.50	397
	4	In front of passengers station port	10.25	147
	5	In front of Egyptian shipbuilding and repair company	10.00	92
	6	In front of Alex. drydock & slipway	4.50	326
Eastern Harbor	7	Vessels anchorage area, out side EH	17.00	342
	8	Entrance of EH, El-Bogaz	9.00	459
	9	Inside EH, fishing boats area	4.00	46
Abu Qir Bay	10	Out side Bay	5.50	66
	11	Vessels anchorage area, inside Bay	11.00	40
	12	In front of Teamssah Shipyard Company	8.75	579
	13	Traffic pathway inside Bay	10.75	52
	14	In front of Petrojet Bay	7.50	536

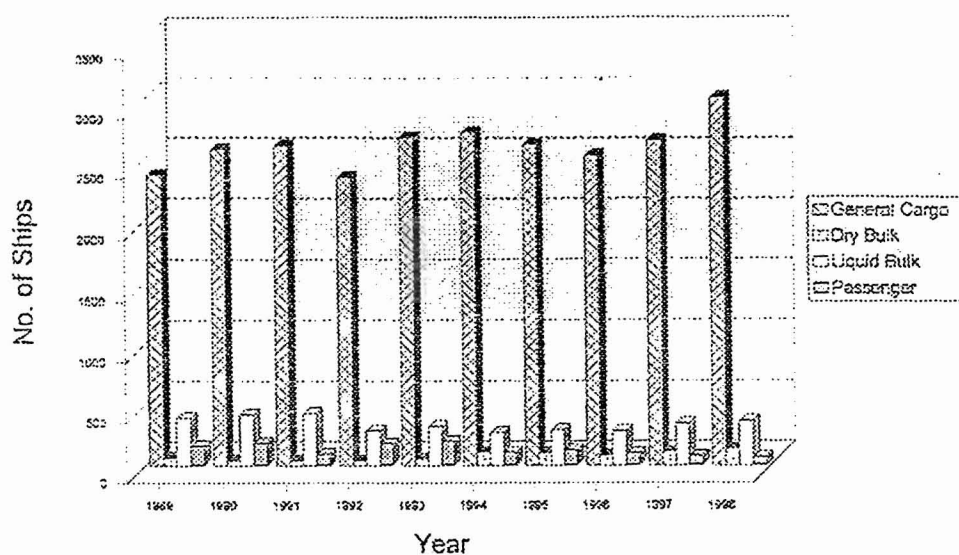


Fig. 2: Number of ships arrived and departure the Western Port of Alexandria between the year 1989-1998 (MRCC, 1995; 1999; 2000)

The overall average of TBT in Abu Qir Bay was  $254.6 \pm 277.1$  ng TBT/L, which was less than the mean concentration of TBT,  $276.3 \pm 186.5$ ,  $293.3 \pm 1475.2$  ng TBT/L in ports of Alexandria, WH and EH, respectively.

Looking at the distribution of TBT in surface water samples, it can be seen that, in WH, the anchorage area have the highest TBT content followed by traffic lane and then the area before the dry and floating docks. Taking in consideration the number of vessels and time spent in the anchorage area.

In Eastern Harbor, the highest concentrations observed near El-Bogaz, where the water is mainly coming from the anchorage area of the WH and some time sewage water of Alexandria city. In Abu Qir, relatively low concentrations of TBT were encountered every where except before the Temssah Shipyard Company with more or less limited effect on the rest of the water in the Bay because of a relative shallowness of waters, the water column was almost homogenous and the TBT concentrations do not vary with depth.

Comparing the concentrations of TBT in the water of Alexandria region with some other areas of the world, it can be seen that, the water in Alexandria region contains higher concentrations of TBT than any other recently reported area. In USA and Japan, the current mean TBT surface concentrations were below 10 ng TBT/L (O'conner, 1996; Cardwell *et al*, 1997) with the exception of a few industrialized area (Evans *et al*, 1995; Carranza *et al*, 1997) and they concluded that US restrictions on TBT usage

## TRIBUTYL TIN CONTAMINATION IN SURFACE WATERS OF THE ALEXANDRIA

significantly reduced TBT loading and on TBT concentrations were not high enough to pose risks of acute toxicity to marine life. In Canada, TBT concentrations in water were found at concentrations between 7 and 66 ng TBT/L (Chau *et al.*, 1997). In Sweden, TBT concentrations in water decreased to levels where no effect on marine periphyton communities could be observed (Dahl, 1996). In UK, the TBT levels were found to be below or near to environmental quality standard (EQS), ng TBT/L for all samples collected from estuarine area (Thomas *et al.*, 2001).

On the other hand, comparing concentrations of TBT in surface water of Alexandria region to the acute and chronic toxicological end points reveals that, the growth inhibition in the clam *Mercenaria*, reported chronic effect 10 ng TBT/L (Lagughlin *et al.*, 1998). In addition the induction of impose in dog welks *N. Lapillus*, occurs at about 1-2 ng TBT/L and sterilization of females is initiated at about 7.3-12.2 ng TBT/L (Brayan *et al.*, 1988; Gibbs *et al.*, 1988). These values were exceeded by TBT concentrations in all 14 seawater samples in which it was found. Consequently, acute toxic effects due to TBT may be expected in those locations.

### CONCLUSIONS

The region of Alexandria is burdened with very heavy marine traffic as well as marine-related industrial activities. Based on the data available for the past 10 years, the number of ships using the port of Alexandria has increased with ca 25%.

Ships today uses to a variable extent, antifouling paints that have TBT as the active antifouling agent. The results were a noticeable increase in the concentrations of TBT in the coastal waters of the region under study, whereby values exceeding 250 ng TBT/L were recorded in the different sub regions.

These values suggest that, antifouling painting is the main source of organo-tin in the Alexandria costal area, although this marine related industrial activity is probably not the only source of TBT contamination. In fact, in heavily polluted or near sewage disposal site, TBT concentration was found insignificant.

In view of the expected increase of numbers of boats navigation the region, the uncontrolled waste discharging and the overloaded maintenance operations are evident that, the TBT concentration will be increased to values that may be dangerous to marine life unless strict measure are taken.

### ACKNOWLEDGEMENT

I would like to express my deepest thanks to Professors Dr. Ali I. Beltagy for his valuable discussion, and also to Dr. Mohamed El-Mamouny for sampling.

REFERENCES

- Dahab, O., 1988. Speciation of tin compounds in sediments of the Alexandria coastal belt, water, Air and Soil Pollut., 40: 433-442.
- Mouk-Dahab, O., 1990. Alkyltin in sediment cores from the Alexandria coastal area, In: Proceedings of the 3 rd international organotin symposium (CIESM / UNEP / FAO / IOC / WHO / IMO / IAEA / CEC), Monaco, 17-20 April, pp. 192-197 (mimeo).
- Bryan, G.W.; Eibbs, P.G. and Burt, G.R., 1988. A comparison of the effectiveness of tri-n-butyltin chloride and five other organotin compounds in promoting the development of imposex in the dogwhelk, *Mucella lapillus*, J. Mar Biol. Assoc., UK 68: 733-744.
- Cardwell, R.D.; Brancato, M.S.; Toll, J.; Deforest-D and Tear, L., 1997. Aquatic ecological risks posed by tributyltin in U.S. surface water: pre-1989-1996 data, submitted to Environmental Toxicological and Chemistry.
- Carranza, M.V.A.; Zomora, M.J.V. and Celaya, V.J., 1997. Organotin compounds in marine water and sediments from the port of Ensenada, Baja California, Scien. Mar., 23(3): 377-394.
- Champ, M.A.; Wade, T.L., 1996. In organotin-Environmental fate and effects, Champ, M.A.; Seligmann, P.F., Eds., Chapman and Hall: London, UK, pp, 55-94.
- Chau, Y.K.; Brown, M.; Yang, F. and Batchelor, S.P., 1997. Occurrence of organotin compounds in the Canadian aquatic environment five years after the regulation of antifouling use of tributyltin, Water Qual. Res. J. Canada, 32(3): 377-394.
- Dahl, B., 1996. On the ecotoxicology of antifouling agents, Ph.D. Thesis. ISBN 91-88896-01-3. Univ. of Gothenburg, Sweden.
- Dowson, P.H.; Bubb, J.M. and Lester, J.N., 1993. Temporal distribution of organotins in the aquatic environment, Mar. Pollut. Bull., 26: 487-494.



*TRIBUTYLTIN CONTAMINATION IN SURFACE WATERS OF THE ALEXANDRIA*

- Evans, S.M., Keksono, T. and Mckinnell, P.D., 1995. Tributyltin contamination: A diminishing problem following legislation limiting the use of TBT-based antifouling paints, *Mar. Pollut. Bull.*, 30: 14-21.
- Gibbs, P.E.; Pascoe, P.L.; Burt, G.R., 1988. Sex change in the female dog whelk, *Nucella lapillus*, induced by tributyltin from antifouling paints, *J. Mar. Biol. Assoc., U*, 68: 715-731.
- Fent, K., 1996. Ecotoxicology of organotin compounds, *Crit. Rev. Toxicol*, 26: 1-117.
- Hall, L.W. and Pinkney, A. E. 1985. Acute and sublethal effects of organotin compounds on aquatic biota: An interpretive literature evolution, *Crit. Rev. Toxicol.*, 14: 159-209.
- Lapota, D.; Rosenbeger, D.E.; Platter-Rieger and Seligman, P.E., 1993. Growth and survival of *Mytilus edulis* Larvae exposed to low levels of dibutyltin and tributyltin, *Mar. Biol.*, 115: 413-419.
- Laughlin, R.B.; Gustafsan, Jr. R.C., and Pendoley, P., 1988. Chronic embryolarval toxicity of tributyltin to early life history stages of the hard-shell clam *Mercenaria mercenaria*, *Mar. Ecol. Progr. Ser.*, 48: 29-36.
- Michel, P. and Averty, B., 1999. Distribution and Fate of tributyltin in surface and deep waters of the Northwestern Mediterranean Environ. Sci. Technol., 33: 2524-2528.
- Michel, P.; Averty, B; Andral, B.; Chiffolleau, J.F. and Galgani, F., 2001. *Mar. Pollut. Bull.*, 42: 1128-1132.
- MRCCI, (1995, 1999, 2000). Activities of the Egyptian ports and Suez Canal, the statistical annual report, the Arab Academy for Science and Technology and Maritime.
- O'Conner, T.P., 1996. Trends in chemical concentrations in mussels and oysters collected along the US coast from 1986 to 1993. *Mar. Environ. Res.*, 2: 183-200.

- Sherman, L.R., and Carlson, T.L., 1980. A modified phenylfluorone method for determining organotin compounds in the ppb and sub ppb range. *J. Anal. Toxicol.*, 4: 31-33.
- Snoeij, N.J.; Penninks, A.H., and Seinen, W., 1987. Biological activity of organotin compounds on overview, *Environ. Res.*, 44: 335-353.
- Stewart, C., 1996. The efficacy of legislation in controlling tributyltin in the marine environment. In: De Moras, J., eds., tributyltin: Case study of an Environmental contamination Cambridge university press. New York, NY, USA. pp. 267-297.
- Takahashi, S.; Tanabe, S., and Kubodora, T., 1997. Butyltin residues in Deep-Sea organisms collected from Suruga Bay, Japan, *Environ. Sci. Technol.*, 31: 3103-3109.
- Thomas, K.V.; Fileman, T.W.; Readman, J.W., and Wolddock, M. J., 2001. Antifouling paint Booster Bodies in the UK coastal Environmental and potential Risks of biological effects, *Mar. Pollut. Bull.*, 42(8): 677-688.
- U.S. Navy, and EPA (Environmental Protection Agency) 1997. Navy program to monitor ecological effects of organotin. Required under the National Defense Authorization Act. For FY, pp.80.