

# Spatio-temporal variation of organotin compounds in seawater and sediments from Cape Town harbour, South Africa using gas chromatography with flame photometric detector (GC-FPD)

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## KEYWORDS

Sediment;  
Antifouling;  
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**Abstract** The spatio-temporal variation of two organotin compounds (OTCs) of tributyltin and triphenyltin in the seawater and sediment of Cape Town harbour was investigated. The organotin compounds were determined by GC-FPD following prior extraction with 0.02% tropolone. The concentration of OTCs varies for locations in Cape Town harbour. The concentration of OTCs in seawater ranges from  $0.067 \pm 0.01$  to  $111.290 \pm 32.20 \cdot 10^{-3}$   $\mu\text{g/l}$  for TBT while that of TPT ranges between between  $\text{ND} \pm \text{SD}$  and  $23008.0 \pm 0.03 \cdot 10^{-3}$   $\mu\text{g/l}$  respectively between locations. Relatively higher concentrations were measured for TBT and TPT during summer than in winter and spring seasons ( $p < 0.05$ ). Apparently, the observed high or low values recorded for TBT in Cape Town harbour could be the result of an increase or decrease in the traffic of ships and boats. TBT was detected in all the sediment samples analysed except for location 9 (entrance to harbour), the two control sites (which are located far away from the inner harbour where boating activities are taking place), and location 12 (Robinson dry dock 2) where the samples were not at all found. For

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the control sites, antifouling compounds TBT and TPT were not detected throughout except for TBT that was found in control A during summer. The seasonal variation of OTC abundance in sediment was also investigated. The results indicated that TBT is present throughout the seasons but is predominantly present in this order summer > winter > spring.

## 1. Introduction

The vast increase in the use of organotin compounds such as tributyltin (TBT) and triphenyltin (TPT) in agriculture and industrial has been generating lot of concerns over the past few years. Among their use as active agents in a wide range of applications include stabilisers in the PVC industry, fungicides, bactericides, antifouling paints, wood preservatives, industrial catalysts, plastic additives and so on (Hoch, 2001; Bhosle, 2006; Okoro et al., 2011). Among these compounds, TBT has been used widely as far back as 1970s when it was being used as a biocide in antifouling paints to prevent aquatic life from being encrusted on marine structures like ship's bottoms, fishing nets, and docks (Alzieu et al., 1989). Therefore, large amounts of organotin compounds have entered coastal waters and their residues have been detected in different organisms, molluscs (Horiguchi et al., 2004), fishes (Takahashi et al., 2000) seabirds (Guruge et al., 1997) seawater (Meena et al., 2009) and marine mammals (Tanabe, 1999). These antifouling paints are the main origin of organotin in marine waters.

Organotins, TBT especially are highly toxic even at lower concentrations (ng/l) to non-target organisms when leached into water (Bhosle, 2007). In a recent finding, exposure of mussel to TBT in a laboratory study showed that the two contributing factors influencing lysosomal responses are exposure concentration and exposure time of TBT (Okoro, 2012). Human exposure to OTCs may have adverse effects on the skin, eyes, liver and on the organ systems such as cardiovascular and gastrointestinal. Bioaccumulation of OTCs thus has great risks which can lead to carcinogenicity and other related effects earlier mentioned. These effects and other associated environmental impacts of OTCs are the reasons why the authorities of many countries have had to restrict the use of TBT as antifouling agents in ship paints and thus target TBT regulation (Abbott et al., 2000). In another related studies, it has been revealed that exposure to organotins can cause imposex in

gastropods and snails (Zhou et al., 2003; Evans et al., 2000; Gomez-Ariza et al., 2006). Among other causes are; growth reduction in mussels (Salazar and Salazar, 1991), larval mortality (Tanabe et al., 2000; Zhou et al., 2003 and immunological dysfunction in fishes (Zhou et al., 2003).

In a related study carried out in South Africa, Imposex in marine invertebrates due to TBT exposure was reported in water from Durban and Richards Bay harbours and Knysna lagoon (David and Anisha, 2003). TBT and triphenyltin (TPT) pollution has also been reported in environmental water samples collected from industrially polluted areas in South Africa, sea water from Port Elizabeth harbour as well as river and dam water samples from the areas around Johannesburg (Ewa et al., 2004). In Johannesburg, high concentrations of dibutyltin (DBT), monobutyltin (MBT) and TBT were recorded in groundwater and sediment samples. Bioaccumulation of organotins was also identified in algae and plant samples (Hermogenes et al., 2009). TBT containing paints are still used to control fouling on the hull of ships and there is no control measure on its usage. In 1997, Taiwan Agricultural Chemicals and Toxic substances Research Institute, Council of Agriculture banned triphenyltin acetate (TPTA) containing pesticides due to its toxicological effects.

OTCs when leached into water, decompose rapidly and tend to have very low mobility and low aqueous solubility; they are adsorbed easily unto suspended particulate matter (SPM) and aggregate more in sediments. OTC degradation is very low and can even last longer for years (Hoch, 2001). Due to the diffusion effects of OTCs on the water column, their bioavailability increased greatly (Diez et al., 2002). TPT is less toxic to TBT, at very low concentrations (ng/kg), OTCs, TBT especially are very toxic to aquatic organisms when they are exposed to these substances. In general, several studies have been conducted on organotin compounds in sediments (Brack, 2002; Chiron et al., 2000; Filipkowska et al., 2011; Biselli et al., 2000; Chem et al., 2010) but no similar study

Table 1 Summary of sampling sites with their coordinates and sampling depths.

Sampling sites	Coordinates	Sampling depth	Description
1	S33 55.053 E18 26.236	14 m	Duncan dock
2	S33 54.982 E18 26.707	12 m	Duncan dock
3	S33 54.571 E18 26.842	14 m	Ben Schoeman dock
4	S33 54.518 E18 27.184		Inside sea 500 m away from point 3
5	S33 54.502 E18 27.566	15 m	Inside sea 500 m away from point 4
6	S33 54.574 E18 25.550	10 m	Duncan dock
7	S33 54.411 E18 25.190	12 m	Robinson dry dock
8	S33 54.535 E18 25.279	14 m	Synchrolift
9	S33 53.827 E18 26.140	8 m	Entrance to harbour
10	S33 53.862 E18 25.809	3 m	Control A
11	S33 53.926 E18 25.496	6 m	Control B
12	S33 54.367 E1825.370	12 m	Robinson dry dock 2

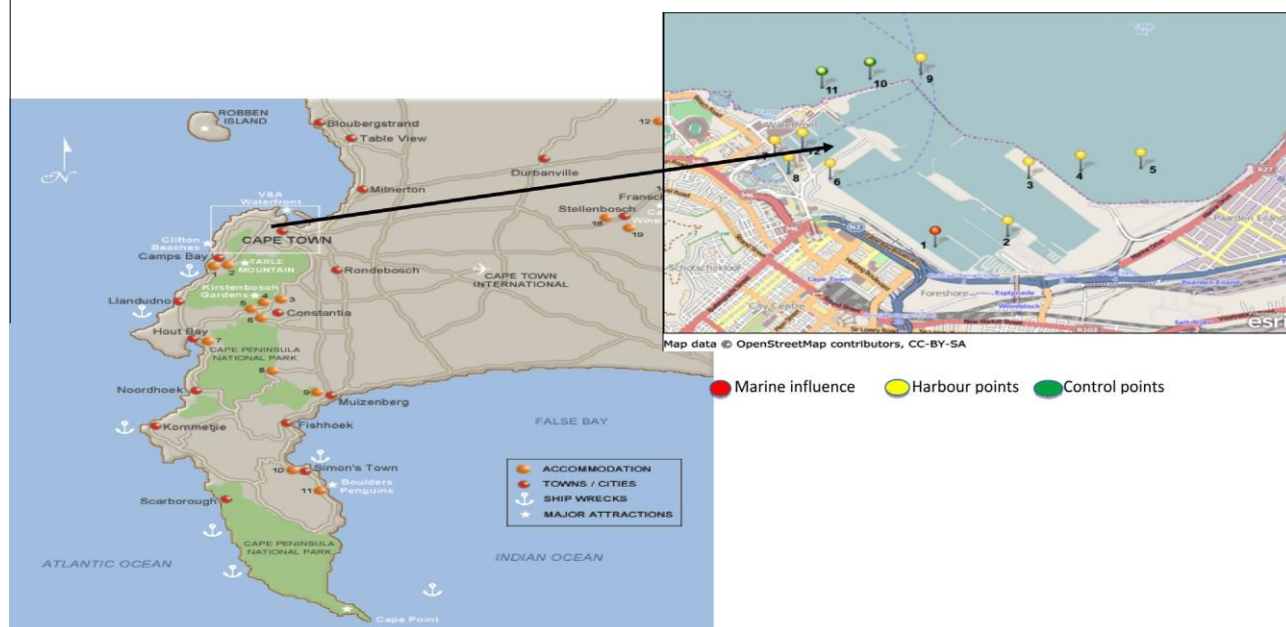


Figure 1 Map indicating the sampling location and sampling points on Cape Town harbour.

has been carried out on Cape Town harbour which is one of the busiest harbours in Africa. Moreover, bans have been placed on the use of TBT as antifouling paints in European countries except in Africa where no standard law against the use of these antifouling paints currently exists. With regard to these, lack of data exists on organotin and its distribution in seawater and sediment of Cape Town harbour. In view of the stated above reasons, the present study was carried out to investigate the spatio-temporal variation of organotin compounds in seawater and sediment from Cape Town harbour, South Africa.

## 2. Materials and methods

### 2.1. Study area

Cape Town harbour is one of the busiest ports in South Africa, handling the largest amount of fresh fruit and second only to

Durban as a port container. The port also has a major repair and maintenance facility, used by several large fishing fleets and ships of West African oil industries. The map of the sampling points in Cape Town harbour is shown in Fig. 1 while Table 1 presents the coordinate of the sampling points. The Cape Town harbour is located within the coordinates of 33°54' S 18°26' E. The port evolved greatly over the centuries and currently consists of several main components. The Ben Schoeman dock is the largest outer dock of the port, where the container terminal is situated. The sediment samples collected at this site were very clayey. The Duncan dock is the smallest and the older inner dock, containing the multipurpose and fruit terminals as well as dry dock, repair quay and tanker basin. Both water and sediment samples at this site are very muddy and oily. The synchrolift dry dock is where the ships are lifted up for repair.

### 2.2. Reagents and working solutions

N-Hexane, methanol, isooctane, and dichloromethane were obtained from Merck (Germany). All organic solvents were of analytical chromatographic grade. They were doubly distilled prior to use. Sodium tetraethyl borate (NaBEt<sub>4</sub>), Glacial acetic acid (98%), sodium acetate, toluene (99%), hydrochloric acid (32%) and anhydrous sodium sulphate were purchased from Sigma – Aldrich South Africa. High purity gases (Helium, Hydrogen and Medical Air (99.999%)) were purchased from Afrox (Pty) Ltd. (South Africa). All glassware used were soaked overnight in 1 M HNO<sub>3</sub> to remove sorbed organotin compounds, and rinsed with milliQ water and acetone immediately before use.

The sodium acetate buffer (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa) was prepared by adding an appropriate amount of sodium acetate (4 g) in Milli Qwater followed by pH adjustment with acetic acid (3 ml in 1 L) to pH (4.5). The working solution of

Table 2 GC-FPD analytical conditions.

Parameter	Setting
Injection port	Split/splitless mode: splitless
Injection volume	1 μl
Injection port temperature	280 °C
Detector temperature	300 °C
Carrier gas – helium flow	1.69 ml/min
Column (Capillary column)	ZB-5MSi (5% phenyl, 95% phenylpolysiloxane, diameters: 30m · 0.25 mm - 0.25 μm film thickness
Oven temperature	50 °C for 1 min then 10 °C to 250 °C for 4 min
Detector type	FPD

sodiumtetraethylborate was freshly prepared in methanol and stored at +4 °C in the refrigerator. Purified water was obtained from MilliQ water system purchased from Millipore (USA).

### 2.3. Instrumentation

Analyses were performed on Shimadzu GC-2010 plus series, Gas chromatography coupled to flame photometric detector (FPD). The GC was equipped with a phenomereX ZB5MSi capillary column (30 m · 0.25 mm I.D · 0.25  $\mu$ m) coated with 5% phenylpolysiloxane. Automated injection was carried out with an auto sampler AOC-20S. Table 2 summarises the GC-FPD analytical conditions.

### 2.4. Other apparatus

The pH was measured using a pH metre with glass electrode from Beckman (Fullerton, USA). A vortex mixer made by Scientific industries Vortex Genie 2 supplied by Lasec, South Africa, and a shaker (Orbishake) supplied by Labotech, Magnetic instrument (FMH instrument) were used.

### 2.5. Organotin determinations in sediments

10 g of air dried sediment was weighed into 250 ml round bottomed flask. 10 g of sodium chloride, 20 ml of milliQwater, 2 ml of conc. HCl, and 20 ml of 0.02% tropolone in methanol and 100 ml of hexane were added in that order. Then, the flask was covered and shaken vigorously for 12 h. The resulting slurry was filtered and collected over anhydrous sodium sulphate to remove water. Extracts were then concentrated on a water bath. Then, the extracts were loaded on silica column for clean up according to the method described by Okoro et al. (2012). Then, ethylation was followed by addition of 1 ml of sodium acetate buffer, and 1 ml of 1% STEB in methanol and the mixture was shaken for 10 min. The extracts were dried over anhydrous sodium sulphate. The final extract was blown to dryness under gentle stream of nitrogen and reconstituted with 1 ml of hexane. 1  $\mu$ l of the final extract was injected for GC-FPD analysis.

### 2.6. Total organic carbon determination

The wet sediment sample was first weighed and then heated in the oven at a temperature of 105 °C for 4 h. 5 g of dried sediment sample was weighed in a crucible and ashed. The ashed sediment sample was then put in the furnace and heated at a temperature of 550 °C overnight (Schumacher 2002).

### 2.7. Organotin determination in seawater (liquid–liquid extraction method)

Three aliquots of 100 mL of water sample were transferred into volumetric flasks and acidified to pH 2. The samples were shaken manually and left to equilibrate for 15 min prior to extraction. This was followed by two consecutive two-minute extractions with 50 ml hexane. The organic layer was collected and derivatised by adding 1 ml of sodium acetate buffer at pH 4.5 and 1 ml of sodium-tetraethyl borate (STEB) in methanol

(1% v/v). The mixture was shaken for 30 min; the organic layer was dried over anhydrous sodium sulphate to remove water. The organic extract was concentrated on a water bath; it was finally blown to dryness under a gentle stream of nitrogen gas and then reconstituted by adding 1 ml of n-hexane. Volumes of 1  $\mu$ l were injected into the GC-FPD instrument for analysis.

### 2.8. Statistical analyses

The results were statistically analysed using SAS 9 software (Cary, NC, USA). Pearson's correlation was applied to evaluate the relationships between the variables and correlation coefficient with  $P \leq 0.05$  was regarded as significant. Principal Component Analysis (PCA) of the data was also carried out using the same software.

## 3. Results and discussion

### 3.1. Concentrations of organotin compounds in seawater

The annual distribution of OTCs around the harbour during the period of September 2011–June 2012 is shown in Table 3 while the concentration of OTCs varies spatially around the harbour (Fig. 2). The concentration ranges from  $0.067 \pm 0.01$  to  $111.290 \pm 32.20 \cdot 10^{-3}$   $\mu$ g/l for TBT while that of TPT ranges between ND  $\pm$  SD and  $23008.0 \pm 0.03 \cdot 10^{-3}$   $\mu$ g/l respectively between locations. The highest concentration of TBT was recorded in location 5 while the least concentration was observed in location 9 (entrance to harbour). TBT was also found in the two control sites in the harbour. A significant variation of  $P \leq 0.05$  was observed from statistical analysis between the locations sampled. The seasonal variation of TBT

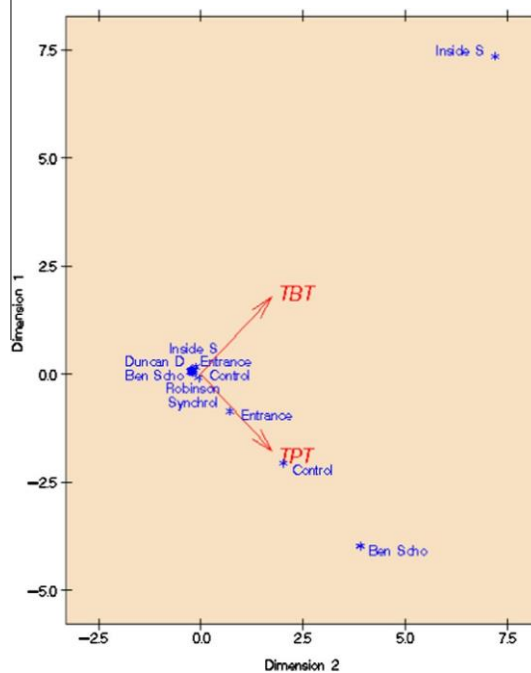


Figure 2 Distribution of TBT in seawater across locations from Cape Town harbour.

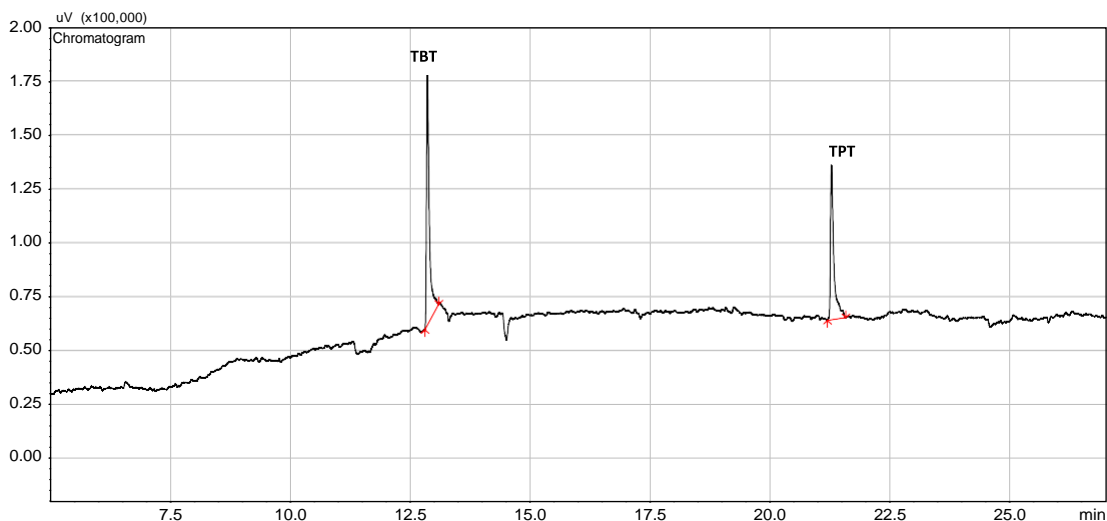


Figure 3 GC-FPD representative chromatogram for organotin compounds in seawater samples from Cape Town harbour, (chromatographic conditions). Retention time: TBT=12.85 min; TPT=21 min.

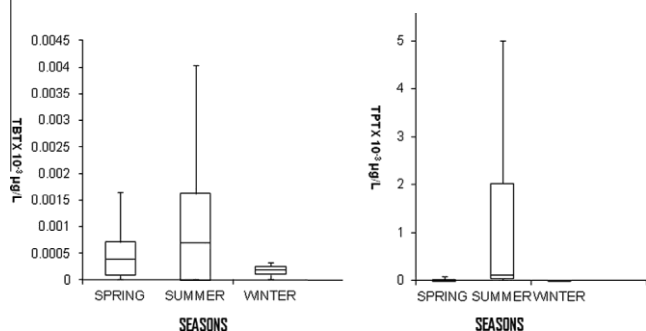


Figure 4 Distribution of TBT in seawater across seasons from Cape Town harbour.

was also investigated, and significant variation of  $P < 0.05$  was also found to exist. We observed a higher concentration of TBT and TPT in summer than in winter and spring. The concentration of TBT varies spatially around harbour. The concentration of TBT varied temporally in the following order: summer > spring > winter as observed in Cape Town harbour. This may indicate that there is some seasonal relationship in the abundance of TBT. Seasonal change has been reported in various studies for water samples and this could be due to seasonal shipping activities in different harbours (Evans and Huggett, 1991; Suzuki et al., 1996; Champ, 2000; Hoch, 2001; Meng et al., 2009). Cape Town harbour is known to have intense shipping activities and is the busiest harbour in Africa. The traffic due to ships and recreational boats is low in winter (June–Sept) and spring and higher in summer (Nov–March) as it appears in the mean season data in Table 3 ( $1.25 \pm 0.33$  Spring;  $27,776 \pm 16.15$  Summer;  $0.154 \pm 0.01$  Winter for TBT and  $41.35 \pm 9.90$  Spring;  $7353.3 \pm 1900.00$  Summer;  $7.684 \pm 3.20$  Winter for TPT). Box and Whisker plot showing the seasonal variation of OTCs in seawater is represented in Fig. 4.

Apparently, the observed high or low values recorded for OTCs in Cape Town harbour could result from an increase

or decrease in the traffic of ships and boats. Dilution due to rising sea water levels in the harbour results in a decrease in the concentration of TBT. High values observed for TBT in summer could be associated to ocean currents and tides. In spring, the spring tide effect may cause high or low TBT concentration, but this also depends on the direction of the tide and ocean currents. The observed highest value of TBT recorded in location 4 (95%) could be as a result of intense ship activities taking place at this location since it is situated inside the harbour, while the least concentration observed for location 9 (entrance to harbour) might be due to less shipping activities taking place at this location. The distribution of TPT varies significantly across locations. Seasonal variation was also observed for TPT. High values were found in Ben Schoeman dock (71%) while the least values were found in location 8 (Synchrolift).

TPT concentration was the highest in summer and lowest in spring. TPT was not detected in winter. High values of TPT recorded in summer could be from various sources along Diep River and wastewater treatment plants that discharge into the harbour. This result is in agreement with a related study by Meng et al. (2009). Their findings showed high TPT concentrations in summer than in winter. The concentrations of metals in Diep River, for example, are much higher because of lower water levels and slower currents (Shuping et al., 2011). Thus, the concentrated waters of the river in summer would contribute to the concentrations in the harbour. In general, a high TPT concentration in summer is due to its use as an antifouling agent in ship painting. It is therefore suggested that adequate regular monitoring of Cape Town harbour should be put in place. More so, it could be of advantage to investigate the toxic effects of this compound to aquatic life with the use of biomarkers since the concentration of  $0.001 \text{ } \mu\text{g/l}$  may be toxic to aquatic life, as indicated earlier (ANZECC, 2000).

### 3.2. Pollution of organotin compounds in sediments

Sediment samples were collected from September 2011 (spring)–June 2012 (winter) at 11 sites in the harbour. The

Table 3 Seasonal and annual mean ( $\pm$ SD) distribution of organotin compounds in seawater from Cape Town harbour.

Item	Seasons				
	Locations	Spring	Summer	Winter	Location mean
TBT (lg/L Mean $\cdot 10^{-6} \pm$ SD $\cdot 10^{-6}$ )	Duncan dock 1	7.50 $\pm$ 2.00	0.723 $\pm$ 0.02	0.290 $\pm$ 0.01	0.588 $\pm$ 0.22
	Duncan dock 2	1.00 $\pm$ 0.00	0.010 $\pm$ 0.01	0.303 $\pm$ 0.05	0.108 $\pm$ 0.15
	Ben Schoeman dock	4.54 $\pm$ 1.78	0.690 $\pm$ 0.38	0.10 $\pm$ 0.01	0.385 $\pm$ 0.04
	Inside sea 1	3.40 $\pm$ 1.20	1.093 $\pm$ 0.60	0.253 $\pm$ 0.02	0.562 $\pm$ 0.49
	Inside sea 2	1.02 $\pm$ 7.47	323.0 $\pm$ 56.00	0.330 $\pm$ 0.07	111.290 $\pm$ 32.20
	Duncan dock 3	4.34 $\pm$ 1.33	0.010 $\pm$ 0.01	0.010 $\pm$ 0.00	0.151 $\pm$ 0.02
	Robinson dry dock	7.05 $\pm$ 3.96	1.00 $\pm$ 0.00	0.243 $\pm$ 0.05	0.320 $\pm$ 0.37
	Synchrolift	0.081 $\pm$ 0.12	0.590 $\pm$ 0.35	0.010 $\pm$ 0.01	0.227 $\pm$ 0.03
	Entrance to harbour	0.010 $\pm$ 0.01	0.010 $\pm$ 0.01	0.180 $\pm$ 0.01	0.067 $\pm$ 0.01
	Control A	0.150 $\pm$ 0.26	3.050 $\pm$ 0.32	0.10 $\pm$ 0.01	1.070 $\pm$ 0.22
	Control B	0.10 $\pm$ 0.01	1.353 $\pm$ 0.42	0.1931 $\pm$ 0.02	0.519 $\pm$ 0.67
	Robinson dry dock 2	1.851 $\pm$ 0.71	2.427 $\pm$ 0.33	0.10 $\pm$ 0.01	1.429 $\pm$ 0.21
	Mean seasons	1.250 $\pm$ 0.33	27.776 $\pm$ 16.15	0.154 $\pm$ 0.01	
	CV5		3.67		
	$P \leq 0.05$		***		***
	Interaction $P \leq 0.05$		***		***
TPT (lg/L mean $\cdot 10^{-6} \pm$ SD $\cdot 10^{-6}$ )	Duncan dock 1	209.0 $\pm$ 0.00	383.0 $\pm$ 28.00	0.010 $\pm$ 0.00	1970.0 $\pm$ 1670.00
	Duncan dock 2	0.010 $\pm$ 0.00	181.98 $\pm$ 2.69	0.010 $\pm$ 0.00	610.0 $\pm$ 92.00
	Ben Schoeman dock	128.0 $\pm$ 0.01	68896.0 $\pm$ 1.00	0.0000 $\pm$ 0.00	23008.0 $\pm$ 0.03
	Inside sea 1	158.973 $\pm$ 27.53	0.010 $\pm$ 0.01	0.010 $\pm$ 0.00	53.0 $\pm$ 15.90
	Inside sea 2	0.010 $\pm$ 0.00	43.273 $\pm$ 7.49	92.103 $\pm$ 79.92	45.0 $\pm$ 6.80
	Duncan dock 3	0.010 $\pm$ 0.00	46.680 $\pm$ 8.08	0.010 $\pm$ 0.00	16.0 $\pm$ 4.70
	Robinson dry dock	0.010 $\pm$ 0.00	50.870 $\pm$ 8.80	0.010 $\pm$ 0.00	0.0000 $\pm$ 0.00
	Synchrolift	0.010 $\pm$ 0.00	45.673 $\pm$ 7.91	0.010 $\pm$ 0.00	15.0 $\pm$ 4.60
	Entrance to harbour	0.010 $\pm$ 0.00	5316.8 $\pm$ 897.50	0.010 $\pm$ 0.00	1772.0 $\pm$ 520.00
	Control A	0.000 $\pm$ 0.00	12345.0 $\pm$ 0.21	0.0001 $\pm$ 0.00	4411.5 $\pm$ 0.122.94
	Control B	0.000 $\pm$ 0.00	931.0 $\pm$ 161.20	0.00 $\pm$ 0.00	310.0 $\pm$ 93.10
	Robinson dry dock 2	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	15.0 $\pm$ 4.60
	Mean seasons	41.347 $\pm$ 9.90	7353.3 $\pm$ 1900.00	7.684 $\pm$ 3.20	
	CV5				
	$P \leq 0.05$		***		***
	$P \leq 0.05$		***		***
Interaction $P \leq 0.05$		***		***	

annual summarised mean data are shown in Table 4. The Cape Town harbour is contaminated with antifouling compounds TBT and TPT. Concentration of OTCs in the samples ranged from 0.010 to 0.829 lg/g for TBT and zero to 0.691 lg/g for TPT. The highest concentration of TBT was recorded in location 3 (Duncan dock). It appears that Duncan dock 3 is heavily polluted due to active recreational boating taking place there. The highest concentration of TPT was recorded at location 7 (Robinson dry dock). This might be due to intensive ship repair activities taking place at this location. TBT was detected in all sediment samples except those collected from location 9 (entrance to harbour), the two control sites (which are located far away from the inner harbour), and location 12 (Robinson dry dock 2). TBT and TPT were not detected from samples collected from the control sites except for TBT that was found in control A during summer. A representative chromatogram showing the OTCs in sediment samples is shown in Fig. 2. Seasonal variation in the concentration of OTCs in harbour sediments was also investigated. The results show that TBT is present throughout the year, but in this order: summer > winter > spring. High concentration values recorded during summer are due to steady flow of water during summer which enhances deposition of TBT in water into the sediment. Low values recorded for TBT and TPT in winter could be due to erosion as a result of an increase in water flow

that removes OTCs from sediments. The representative chromatograms of OTCs in water and sediment samples are shown in Figs. 3 and 5.

Principal component analysis (PCA) was used for data analysis. The tests revealed that TPT concentration was significantly high in summer while TBT was more predominant in winter. Significant variation of  $P \leq 0.05$  was calculated for the seasonal effects of TPT and TBT (Fig. 6). PCA was also used to estimate the effect of locations on the OTCs investigated (Fig. 7) and a significant variation of  $P \leq 0.05$  was obtained while an insignificant correlation was found from the statistical analysis. TBT and TPT were predominantly found in Robinson dry dock and Duncan dock. The highest annual percentage distribution for TPT was recorded in locations 3 (82%) and (7) 6%. The result suggests that the major inputs of TBT and TPT at Robinson dry dock and Duncan dock come from shipping activities such as ship building and repair activities (Chem et al., 2010). Significant correlation of  $P \leq 0.05$  was found for all the seasons. Insignificant correlation of  $P > 0.05$  was found for TPT and TBT, respectively. For TBT an average concentration of more than 90% was recorded annually in location 4.

From this study, Triphenyltin, which is a co-toxicant to antifouling compound TBT, was found in some sample but generally lower than that of TBT. TBT was generally found

Table 4 Annual mean ( $\pm$ SD) concentration of organotin compounds in sediments from Cape Town harbour.

Item	Seasons				
	Locations	Spring	Summer	Winter	Location mean
TBT (g/L Mean $\cdot 10^{-6} \pm$ SD $\cdot 10^{-6}$ )	Duncan dock 1	0.035 $\pm$ 0.0577	0.010 $\pm$ 0.00	0.048 $\pm$ 0.00	0.017 $\pm$ 0.014
	Duncan dock 2	ND	ND	0.023 $\pm$ 0.00	0.014 $\pm$ 0.006
	Ben Schoeman dock	0.014 $\pm$ 0.002	0.01 $\pm$ 0.00	ND	0.011 $\pm$ 0.002
	Inside sea 1	NF	ND	0.033 $\pm$ 0.001	0.018 $\pm$ 0.013
	Inside sea 2	NF	ND	0.001 $\pm$ 0.00	0.010 $\pm$ 0.00
	Duncan dock 3	0.001 $\pm$ 0.00	0.001 $\pm$ 0.00	2.467 $\pm$ 0.153	0.829 $\pm$ 1.231
	Robinson dry dock	0.022 $\pm$ 0.002	0.016 $\pm$ 0.007	0.001 $\pm$ 0.00	0.063 $\pm$ 0.071
	Synchrolift	0.044 $\pm$ 0.003	0.028 $\pm$ 0.001	0.001 $\pm$ 0.00	0.027 $\pm$ 0.15
	Entrance to harbour	ND	ND	ND	ND
	Control A	ND	0.087 $\pm$ 0.00	ND	0.036 $\pm$ 0.038
	Control B	ND	ND	ND	ND
	Robinson dry dock 2	NF	NF	NF	NA
	Mean seasons	0.016 $\pm$ 0.01	0.030 $\pm$ 0.011	0.022 $\pm$ 0.069	
	CV5				
	$P < 0.05$		***		***
	Interaction $P < 0.05$		***		
	TPT (g/L mean $\cdot 10^{-6} \pm$ SD $\cdot 10^{-6}$ )	Duncan dock 1	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00
Duncan dock 2		0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00
Ben Schoeman dock		0.010 $\pm$ 0.01	0.010 $\pm$ 0.00	0.0000 $\pm$ 0.00	0.010 $\pm$ 0.00
Inside sea 1		NF	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00
Inside sea 2		NF	0.010 $\pm$ 0.00	0.001 $\pm$ 0.00	0.010 $\pm$ 0.00
Duncan dock 3		0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00
Robinson dry dock		0.010 $\pm$ 0.00	2.052 $\pm$ 0.171	0.010 $\pm$ 0.00	0.691 $\pm$ 0.010
Synchrolift		0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00	0.010 $\pm$ 0.00
Entrance to harbour		ND	ND	ND	ND
Control A		ND	ND	ND	0.010 $\pm$ 0.00
Control B		ND	ND	ND	0.010 $\pm$ 0.00
Robinson dry dock 2		NF	NF	NF	NA
Mean seasons		0.010 $\pm$ 0.00	0.018 $\pm$ 0.574	0.010 $\pm$ 0.00	
CV5					
$P < 0.05$			***		
$P < 0.05$			***		***
Interaction $P < 0.05$			***		

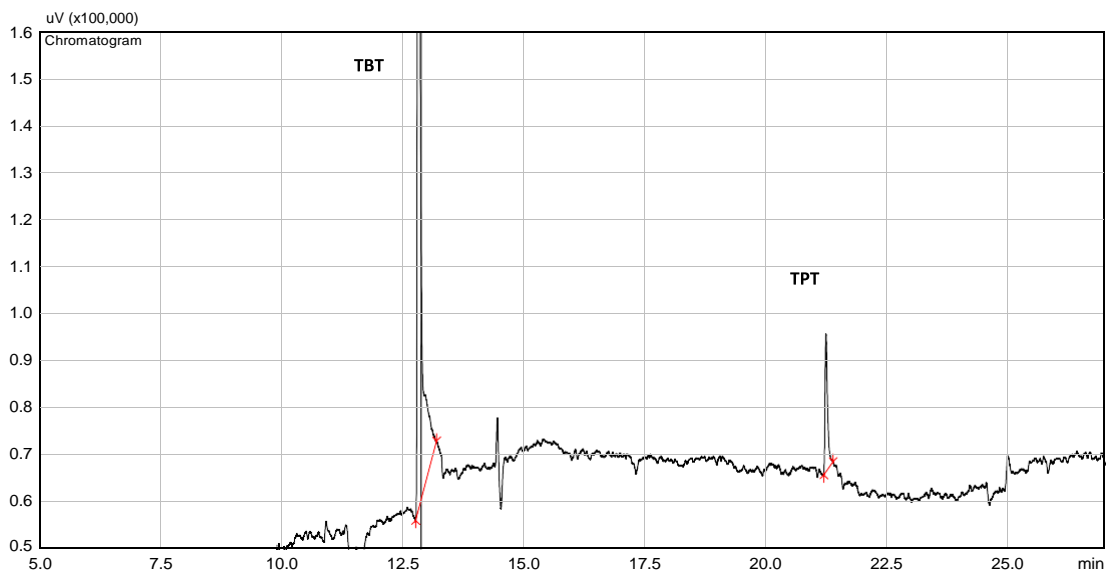


Figure 5 GC-FPD representative chromatogram for organotin compounds in sediment samples from Cape Town harbour.

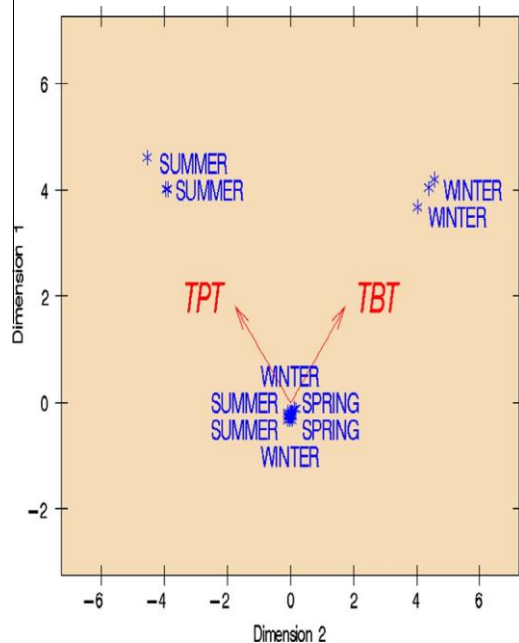


Figure 6 Principal component analysis showing seasonal variation of organotin compound.

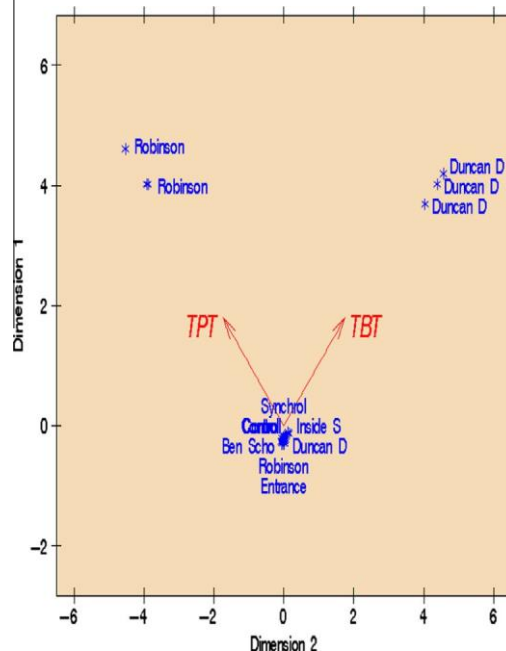


Figure 7 Principal component analysis showing distribution of organotin compounds across locations.

in all locations except in locations 9, 11, and 12 which are further away from the harbour activity. High TPT levels that occurred at location 7 indicate a considerable input and persistent in the sediment samples. Previous studies show high concentration levels of OTCs, especially TBT, in marine sediments, and this has also been found for freshwater sediments (Fent and Muller, 1991; Fent and Hunn, 1995; Langston and Popoe, 1995; Biselli et al., 2000).

3.3. Total organic carbon

The annual mean concentration recorded during the study period ranged from 1.398% to 15.135% as shown in Table 5. The highest value was recorded in location 2 (Duncan dock). This high result suggests that intensive ship repair, painting and

other boating activities taking place at this location might be the source of elevated values of TOC at this location (Mzoughi et al., 2005). A significant difference of  $p \leq 0.05$  was observed between the seasons. High TOC values were recorded during summer. This might be due to stable or steady flow of water during summer and in which most of the organic matter is leached into the sediments.

4. Conclusion

TBT was detected in all the sediment samples analysed except for location 9 (entrance to harbour), the two control sites (which are located far away from the inner harbour where boating activities are taking place), and location 12 (Robinson dry dock 2) where the samples were not found at all. The seasonal

	Locations	Seasons			Location mean
		Spring	Summer	Winter	
TOC	Duncan dock 1	3.57 ± 0.98	19.3 ± 24.06	1.0335 ± 0.002	11.435 ± 8.305
	Duncan dock 2	3.45 ± 1.01	26.82 ± 30.25	1.031 ± 0.0014	15.135 ± 11.038
	Ben Schoeman dock	1.47 ± 0.22	26.47 ± 32.98	1.032 ± 0.001	13.97 ± 11.83
	Inside Sea 1	1.04 ± 0.22	25.32 ± 17.96	1.031 ± 0.002	13.177 ± 8.718
	Inside Sea 2	0.17 ± 0.125	4.57 ± 4.43	1.0305 ± 0.001	2.845 ± 1.624
	Duncan dock 3	7.62 ± 5.47	18.165 ± 0.10.71	1.0305 ± 0.001	12.893 ± 4.618
	Robinson dry dock	5.93 ± 1.52	11.115 ± 5.35	1.032 ± 0.001	8.525 ± 2.194
	Synchronolift	3.95 ± 0.04	1.105 ± 0.014	1.031 ± 0.00	2.527 ± 0.822
	Entrance to harbour	0.49 ± 0.014	2.305 ± 1.265	1.034 ± 0.002	1.398 ± 0.638
	Control A	0.365 ± 0.07	11.56 ± 0.00	1.031 ± 0.00	5.96 ± 3.2318
	Control B	0.725 ± 0.77	8.91 ± 0.00	1.031 ± 0.00	4.81 ± 2.373
	Mean seasons	2.702 ± 0.573	14.149 ± 3.25		
	CV5		3.67		
$P \leq 0.05$		***		***	
Interaction $P \leq 0.05$		***			



variation of OTC abundance in sediment was also investigated, the results indicated that TBT is present throughout the seasons but predominantly in this order summer > winter > spring. High variation recorded during summer is associated to the steady flow of water during summer which enhances siltation of TBT in water column into sediment. The least value recorded for TBT and TPT in winter could be as a result of erosion due to increase in water flow. Ocean tidal effect might be the reason while the least value was recorded during spring throughout the studies. The annual distribution of OTCs in the seawater and sediments of Cape Town harbour has been investigated. Apparently, the observed high or low value recorded for TBT compound in Cape Town harbour could be as a result of increase or decrease in the traffic of ships and boats. Another reason could be as a result of the natural dilution of the harbour water during winter and spring periods.

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