



## Environmental behavior of organotin compounds in the coastal environment of Xiamen, China

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### ABSTRACT

In 2006, organotins pollution were investigated in the coastal environment of Xiamen, China. Six species of organotin compounds including tributyltin, triphenyltin and their degradation compounds were quantified in the dissolved and particulate phases of the water, and in the sediment using GC-FPD. The concentrations of organotin compounds ranged from 2.2 to 160 ng (Sn) L<sup>-1</sup> dissolved in the water, 0.14–6.7 ng (Sn) L<sup>-1</sup> in suspended particulate matter and  $\sim 26$  ng (Sn) g<sup>-1</sup> (dry weight) in the sediment. The highest concentration of total organotin or tributyltin in water was found in a shipyard and at a station near the inlet of the harbor, indicating fresh inputs of antifouling paints to Xiamen's coastal environment. Organotin speciation was performed on sediment cores to investigate contamination trends over the past ten years in the harbor. The results of <sup>210</sup>Pb dating indicated that Xiamen western harbor suffered contamination during 2000. The environmental behavior of organotins such as the enhancement of the microlayer, partitioning between water/suspended particulate matter and between water/sediment are also discussed in this paper.

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### 1. Introduction

Environmental concerns about organotin (OT) compounds have increased remarkably during the past 20 years, due to the large use of these compounds (Hoch, 2001). Tributyltin (TBT), one of the most toxic compounds used as an active component in antifouling paints, was introduced to the marine environment through human activities. It can be found in many coastal waters in both industrial and developing countries with the highest levels in harbors and shipping lanes (Basheer et al., 2002; Bhosle et al., 2004; Sudaryanto et al., 2002, 2004). The detrimental effects of TBT on oyster (Alzieu et al., 1991; Alezieu, 2000), dogwhelk (Bryan et al., 1988), mussel (Salazar and Salazar, 1991) and microalgae (Beaumont and Newman, 1986) at low nanomole aqueous concentrations are well determined. In some developed countries, the use of TBT-based antifouling paints has been banned for 10–20 years. Although a reduction of OT contamination is recorded, TBT is still persistent in marine coastal water and sediment, particularly in sea areas with frequent boat activities (Morcillo and Porte, 1998). The ubiquitous existence of TBT and its breakdown products could be detected in fish from the deep-sea environment as a result of long range transport and bioaccumulation (Takahashi et al., 1997; Veronica and Cinta, 2002; Harino et al., 2005).

In China, as in other Asian countries except Japan and the Hong Kong Special Administrative Region of China, there is no specific

legislation controlling the use of TBT (Champ, 2000). In part this is probably because the complex procedures of sample preparation, the expensive sensitive instruments involved and the trace levels of OT compounds found enlarge the difficulties of TBT analysis in seawater. There are few data evaluating the pollution status in the marine environment of China. Although Xu and Jiang (1999) developed an analytical method for OT compounds, and Jiang et al. (2001) and Huang et al. (2005) investigated some important harbors and estuaries of China, the environmental behavior and the risk assessment of OT have not been integrally studied in the marine environment of China.

In order to evaluate the status of OT contamination, the chemistry and behavior of these compounds in the coastal environment, and to verify the effectiveness of legal provisions adopted by the Chinese government, the present paper studied the speciation, concentration, spatial and temporal variations of OT compounds including TBT, triphenyltin (TPHT) and their breakdown products, monobutyltin (MBT), dibutyltin (DBT), monophenyltin (MPHT) and diphenyltin (DPhT), in seawater, suspended particulate matter (SPM) and sediment from the coastal waters of Xiamen, China.

### 2. Materials and methods

#### 2.1. Study area

Xiamen western harbor is one of the major hinge ports in the southeast of China. The harbor is a semi-enclosed bay with a

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coastline of about 30 km and water depths ranging from 6 to 25 m. The rapid development of the Xiamen Economic Special Zone since 1986 has resulted in significant stress to Xiamen environments. More than 50 million tons of ore are received and exported through the harbor annually. Additionally, a shipyard, dry dock facility, and military and fishing boats are located in the port. The highest levels of imposex are found in some sensitive gastropod species in Xiamen western harbor (Shi et al., 2002). Thus, OT pollution in Xiamen harbor should not be neglected.

## 2.2. Sample collection

A research vessel, Haiyang I, owned by the College of Oceanography and Environment, Xiamen University, was used to collect seawater and sediment samples from various locations in the Xiamen sea area during March 2006, and the collection sites are shown in Fig. 1.

The surface seawater samples were collected at a depth of ~0.5 m with a Niskin water sampler (2 L capacity). The 300–500  $\mu\text{m}$  thick microlayer water was collected using a steel-sieve sampler. Bottom water and surface sediments were collected using a Niskin water sampler bind with a grab with a capacity of 1 kg, which was 1 m away from the water sampler. Sediment cores were collected using a self-designed instrument with a 50 cm PVC tube and a 10 kg lead block.

Water samples were immediately filtered through GF/F filters (0.7  $\mu\text{m}$ , 90 mm, Whatman, UK) to remove suspended particles (the SPM). Then hydrochloric acid (HCl, 1 M, 2 mL) was added into the dissolved seawater as a preservative. The mixtures were stored in 1 L acid-washed amber glass bottles and kept in a refrigerator (4 °C) for later chemical analysis. The 3–4 cm sediment cores were cut into several pieces on the boat immediately. Then the sediment and SPM samples were wrapped in pre-baked aluminum foil (450 °C for 4 h), transferred to polyethylene bags and kept in an icebox. After sampling finished, the SPM and sediment samples were transported to the laboratory and stored at –20 °C until analysis.

In the present study, 17 surface water samples, 6 microlayer water samples, nine bottom water samples, nine surface sediment

samples and three sediment cores were collected from 17 typical coastal sites along the coast of Xiamen.

## 2.3. Chemicals and Instruments

Standards of the OT compounds, MBT, DBT, TBT, MPhT, DPhT, TPhT, the internal standard (IS) tripropyltin (TPrT) and the derivative sodium tetraethyl borate (STEB), with purity >98%, were purchased from Aldrich, USA. Methanol, dichloroform and other chemical solvents involved in the experiments were all of HPLC-grade, ordered from TEDIA, USA.

The solid phase extraction (SPE) columns used in the experiment were SUPELCO ENVI™-C18 SPE Tubes (3 mL, 5 mg). The solid phase microextraction (SPME) holder and the fibers coated with 100 mm thickness polydimethylsiloxane were obtained from SUPELCO (Bellefonte, PA, USA).

## 2.4. Analytical procedure

In order to eliminate the problem of high background levels due to analyte adsorption on glassware surfaces, each piece of glassware was soaked in 2% nitric acid overnight and rinsed several times with hot tap water, and then rinsed three times using Milli-Q water.

**Seawater:** OT compounds were extracted from the seawater samples following the method of Ikonomou et al. (2002). 800 mL seawater samples were measured into a 1000-mL bottle. TPrT as IS, and 50 mL NaOAc buffer (adjusted to pH 5.4 by adding AcOH) was added to each sample. After shaking, STEB in methanol (1%, v/v) was added to each sample. Samples were immediately shaken for 1 min, then the sample extraction was transferred to the SPE column, the analytes eluted with 5 mL of hexane/ethyl acetate (3:1, v/v), 5 mL hexane and 1 mL benzene, and the elution was collected. It was dried over anhydrous sodium sulphate, concentrated to 0.1 mL using nitrogen gas prior to GC analysis.

**SPM:** A filter with SPM was weighed into a 60-mL glass vial. TPrT was added as the IS, and then glacial acetic acid, NaOAc buffer (pH 5.5) and NaCl was added to sample. The acidic mixture was extracted with hexane (with tropolone, 0.02%) by shaking for 10 min. Subsequently, each sample was centrifuged at 3000 rpm for 5 min and the organic layer was transferred to a 15-mL glass centrifuge tube. The extraction with the tropolone solution was repeated, and the final extract was combined with the former in the glass centrifuge tube. The extracts were reduced to 2 mL under nitrogen gas and then STEB in methanol (1%, v/v) was added. The solutions were vortexed, an additional aliquot of STEB was added and the solutions were vortexed again. After 15 min, NaOH was added and the samples were transferred/extracted with hexane/ethyl acetate (3:1, v/v) and hexane. The organic layer was collected and dried over anhydrous sodium sulphate, concentrated to 0.1 mL using nitrogen gas prior to GC analysis.

**Sediment:** OT compounds were extracted from the sediment samples following the method of Millan and Pawliszyn (2000). 1–2 g of sediment was accurately weighed and placed in a 10 mL centrifugation glass vial, and TPrT as IS was added. In order to leach the OTs from the sediment, 8 mL of a mixture of 20% hydrochloric acid–methanol (1:1) was carefully added. The mixture was sonicated for 1 h (47 kHz frequency) and centrifuged at 3000 rpm for 5 min. The centrifuged solution was mixed with 20 mL of a sodium acetate buffer solution (pH 5.0; 2 M) in a glass vial sealed with a septum and placed in a water bath at 40 °C for 15 min. A 1.5 mL volume of STEB (1%) was later added to the vial and it was maintained for 2 min at 700 rpm. Maintaining the same extractions conditions (700 rpm, 40 °C), the SPME fiber was exposed to the headspace for 15 min. After sampling, the fiber was removed and

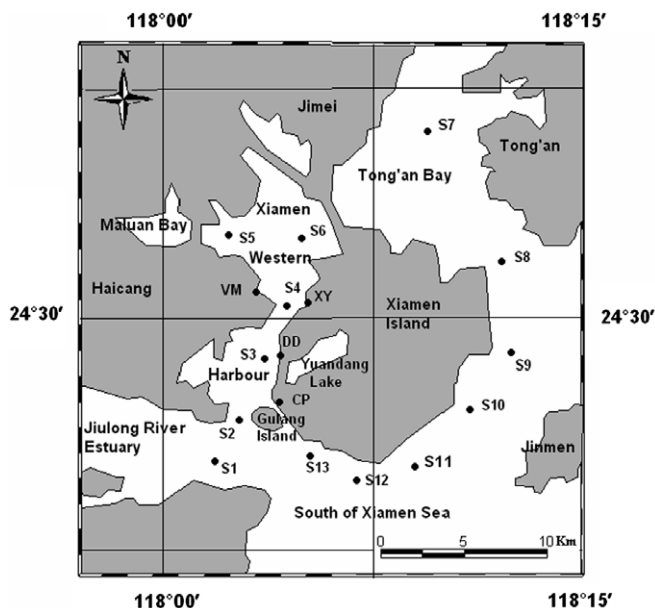


Fig. 1. Map of sampling stations in the Xiamen sea area (VM—Shipyard Port; XY—Xiangyu Port; DD—Dongdu Port; CP—Custom Port).

inserted into the injector port. The desorption temperature and time were 230 °C and 4 min, respectively.

2.5. Instrumental analysis

A capillary gas chromatograph (Agilent HP 6890 plus) equipped with a flame photometric detector (FPD), a tin-specific filter (610 nm) and HP-5 capillary column (30 m, 0.32 mm i.d.) was used to separate and quantify the OT compounds. The initial oven temperature was 60 °C. After 2 min, the oven temperature was raised to 230 °C at the rate of 20 °C min<sup>-1</sup> and was held at this temperature for 2 min. The injector was used in track oven mode while the FPD was maintained at 250 °C. Helium was used as a carrier gas (1.9 mL min<sup>-1</sup>). Hydrogen and air flows were maintained at 120 and 100 mL min<sup>-1</sup>, respectively. Quantification of each peak was done using the data handling system installed in the instrument.

2.6. Quality control

Using Milli-Q water and silica sand powder spiked with known concentrations of mixed standard solution were passed through the entire analytical procedure. The recovery and the detection limit of each speciation of OT compounds are shown in Table 1. CRM462 (No. 255, EUR) was used to validate the sediment extraction method. DBT and TBT concentrations of 43 ± 2.8, 70 ± 1.4 µg kg<sup>-1</sup> (dw) were found in CRM462. The results obtained for DBT and TBT were in good agreement with the certified values of 54 ± 15 and 68 ± 12 µg kg<sup>-1</sup> (dw).

3. Results and discussion

3.1. Speciation and concentration of organotin compounds

In the marine environment, TBT and TPhT undergo microbial- and photodegradation and can be decomposed to DBT and MBT, or DPhT and TPhT, then to Sn(IV). In this study, six OT compounds including TBT and TPhT and their degradation compounds were quantified simultaneously in seawater and sediment. From Tables 2 and 3, it is seen that speciation and concentration of OT compounds were variable in the dissolved and particulate phases of the microlayer, subsurface and bottom water, and the surface sediment from the Xiamen sea area. MBT was a predominant compound in the dissolved phase of the microlayer and bottom water, and in the sediment. TBT was found mainly in the surface sediment, microlayer and particulate bottom water. Phenyltin compounds were also found in particulate surface water rather than dissolved in water and in the sediment. This partitioning pattern of OT compounds is most related to the location and the point of sources, and also due to the properties of OT species. Lower level of TBT in water suggests its low residence time in water than sediment. However, the partitioning pattern for MBT dominated in the sediment may indicate that MBT not only from

Table 1 Recovery and detection limit of the organotin compounds analytical method

	Seawater	Detection limit	Sediment	Detection limit
	Recovery (%)	(ng (Sn) L <sup>-1</sup> )	Recovery (%)	(ng (Sn) g <sup>-1</sup> dw)
MBT	65	0.09	116	0.19
DBT	74	0.11	93	0.09
TBT	93	0.06	122	0.08
MPhT	80	0.11	116	0.11
DPhT	82	0.05	92	0.03
TPhT	89	0.05	98	0.25

Table 2 Concentration of organotin compounds dissolved in seawater of the Xiamen area (ng (Sn) L<sup>-1</sup>)

	Microlayer water						Surface water						Bottom water														
	MBT	DBT	TBT	MPhT	DPhT	TPhT	MBT	DBT	TBT	MPhT	DPhT	TPhT	MBT	DBT	TBT	MPhT	DPhT	TPhT	ΣBTS	ΣPHTs	ΣPHTs	ΣBTS	ΣPHTs	ΣPHTs			
S1							12	nd	0.44	nd	nd	0.24	12	nd	0.44	nd	nd	0.24	12	nd	0.24	12	nd	0.24	12	nd	0.24
S2							2.9	nd	nd	nd	nd	nd	2.9	nd	nd	nd	nd	nd	2.9	nd	nd	2.9	nd	nd	2.9	nd	nd
S3							10	nd	nd	nd	nd	nd	10	nd	nd	nd	nd	nd	10	nd	nd	10	nd	nd	10	nd	nd
S4							2.7	nd	nd	nd	nd	nd	2.7	nd	nd	nd	nd	nd	2.7	nd	nd	2.7	nd	nd	2.7	nd	nd
S5	13	nd	nd	nd	0.7	nd	7.9	nd	nd	nd	nd	0.22	7.9	nd	nd	nd	nd	0.22	7.9	nd	0.22	7.9	nd	0.22	7.9	nd	0.22
S6	25	nd	60	nd	nd	nd	2.2	nd	nd	nd	nd	nd	2.2	nd	nd	nd	nd	nd	2.2	nd	nd	2.2	nd	nd	2.2	nd	nd
S7	17	nd	9.6	nd	nd	0.87	12	nd	nd	nd	nd	nd	12	nd	nd	nd	nd	nd	12	nd	nd	12	nd	nd	12	nd	nd
S8	29	nd	nd	nd	nd	nd	3.6	0.51	nd	0.61	nd	nd	3.6	0.51	nd	0.61	nd	nd	3.6	0.51	nd	3.6	0.51	nd	3.6	0.51	nd
S9	13	nd	7.4	3	nd	nd	12	nd	nd	0.53	nd	0.19	12	nd	nd	0.53	nd	0.19	12	nd	0.19	12	nd	0.19	12	nd	0.19
S10							12	nd	nd	nd	nd	0.33	12	nd	nd	nd	nd	0.33	12	nd	0.33	12	nd	0.33	12	nd	0.33
S11							12	nd	0.47	nd	0.25	nd	12	nd	0.47	nd	0.25	nd	12	nd	0.25	12	nd	0.25	12	nd	0.25
S12							15	nd	0.33	nd	nd	nd	15	nd	0.33	nd	nd	nd	15	nd	nd	15	nd	nd	15	nd	nd
S13							11	nd	nd	nd	nd	nd	11	nd	nd	nd	nd	nd	11	nd	nd	11	nd	nd	11	nd	nd
VM	57	4.8	4.2	nd	7.9	nd	61	49	3.5	46	nd	nd	61	49	3.5	46	nd	nd	61	49	nd	61	49	nd	61	49	nd
CP							67	8	nd	46	nd	nd	67	8	nd	46	nd	nd	67	8	nd	67	8	nd	67	8	nd
XY							25	7.3	nd	nd	nd	nd	25	7.3	nd	nd	nd	nd	25	7.3	nd	25	7.3	nd	25	7.3	nd
DD							64	nd	nd	nd	16	nd	64	nd	nd	nd	16	nd	64	nd	nd	64	nd	nd	64	nd	nd

nd: Not detected.

**Table 3**  
Concentration of organotin compounds in seawater SPM and surface sediment from the Xiamen area

		SPM (g L <sup>-1</sup> )	MBT	DBT	TBT	MPhT	DPhT	TPhT	∑BTs	∑PhTs
Surface Water (ng (Sn) L <sup>-1</sup> )	S9		nd	nd	nd	6.4	nd	0.38	0	6.8
	S10	0.04	nd	nd	nd	nd	1.9	0.19	0	2.1
	S11	0.05	nd	nd	nd	nd	nd	0.26	0	0.26
	S12	0.03	nd	nd	nd	nd	nd	0.14	0	0.14
	S13	0.04	nd	nd	nd	nd	nd	0.49	0	0.49
Bottom Water (ng (Sn) L <sup>-1</sup> )	S10	0.13	nd	nd	20	nd	nd	nd	20	0
	S11		nd	nd	3.0	nd	nd	0.51	3.0	0.51
	S12	0.10	nd	5.3	nd	nd	nd	0.80	5.3	0.80
	S13		nd	4.3	nd	nd	nd	nd	4.3	0
Surface Sediment (ng (Sn) g <sup>-1</sup> dw)	S2		60	3.1	0.18	nd	nd	nd	63	0
	S4		115	2.8	0.45	nd	nd	nd	118	0
	S5		70	3.4	0.52	1.1	nd	nd	74	1.1
	S7		16	1.2	0.17	0.19	nd	nd	17	0.19
	S8		30	0.95	26	nd	16	1.00	57	17
	S9		39	2.2	nd	nd	nd	nd	41	0
	S10		103	1.7	1.0	nd	nd	nd	106	0
	S12		74	nd	nd	nd	nd	nd	74	0
	S13		78	0.44	0.36	nd	nd	nd	79	0

nd: Not detected.

the dominant breakdown product of TBT degrading, but also come from other sources, such as city sewage, industry wastewater etc. It has been known that MBT was used as stabilizers in polyvinyl chloride (PVC) and as catalysts in the production of polyurethane foams, silicones, and in various industrial processes.

The concentrations of total butyltin compounds (∑BTs) in the dissolved water of the surface microlayer, subsurface layer and bottom layer ranged between 13–85, 2.2–114 and 10–36 ng (Sn) L<sup>-1</sup>, respectively. ∑BTs of SPM was 3.0–20 ng (Sn) L<sup>-1</sup> in bottom water. ∑BTs in the surface sediment varied from 17 to 120 ng (Sn) L<sup>-1</sup>. TBT was detected mainly in microlayer water (nd ~ 60 ng (Sn) L<sup>-1</sup>) and sediment (nd ~ 26 ng (Sn) g<sup>-1</sup> dw). Butyltin compounds were not found in the SPM of surface water. The concentrations of total phenyltin compounds (∑PhTs) in the dissolved water of the surface microlayer, subsurface layer and bottom layer ranged between 0–7.9, 0–46 and 0–1.3 ng (Sn) L<sup>-1</sup>, respectively. ∑PhTs of SPM were 0.14–6.8 ng (Sn) L<sup>-1</sup> in surface water and 0–0.80 ng (Sn) L<sup>-1</sup> in bottom water. ∑BTs in the surface sediment varied from 0 to 17 ng (Sn) L<sup>-1</sup>. The highest concentration of butyltin compounds or TBT was found in the shipyard and station S5 (inlet of the harbor), indicating fresh inputs of antifouling paints from the shipyard and mariculture in Xiamen's western harbor. The values of OTs in the ship navigation lanes (S4) and at the outlet of the harbor (S2) were lower. The presence of TPhT and its degradation products MPhT and DPhT in the water also originated from the use of antifouling paints from the foreign imported and exported ships in Xiamen harbor. Even, the levels of container transport for Xiamen's global trade have increased from 2 million TEUs (standard container capacity measure of 20-foot equivalent units) in 2004 to around 4 million TEUs in 2006, the difference contamination of BTs and PhTs in the degree of their magnitude in Xiamen indicated that the local sources of butyltin compounds were dominant with the less phenyltin compounds input.

According to previous results which show that TBT concentration ranges from <0.5 to 976.9 ng (Sn) L<sup>-1</sup> in Chinese coastal waters (Jiang et al., 2001), and compared with the results from the Gulf of USA marine estuaries (<2–9 ng L<sup>-1</sup>, Larsen et al., 1997), Singapore coastal water (3210 ng L<sup>-1</sup> mean, Basheer et al., 2002), the coast of western Japan (21 ng L<sup>-1</sup> mean, Murai et al., 2005) and the west coast of India (370–120 ng L<sup>-1</sup> in dissolved water, 0.6–8.3 ng L<sup>-1</sup> in SPM, Bhosle et al., 2004, the Xiamen sea area was lightly contaminated by OTs.

Based on the UK Environment Quality Target value for seawater of 2 ng TBT L<sup>-1</sup> (UK Department of the Environment, 1989), the US

EPA Aquatic Life Advisory Concentration of 10 ng TBT L<sup>-1</sup> (US EPA, 1985), and the Australian sediment quality guidelines for TBT of 5 ng g<sup>-1</sup> and 70 ng g<sup>-1</sup> for low and high trigger values (ANZECC/ARMCANZ, 2000), most of the water and sediment samples from the Xiamen sea area were in the safety range, but the seawater at station S5 and the shipyard; particulate bottom water at S10, S11 (Southeast of Xiamen); and surface sediment at station S8 (outlet of Tong'an Bay), exceeded the standard and were a risk to benthic organisms.

### 3.2. Enrichment of surface microlayer

The microlayer can have enriched concentrations of potentially toxic chemicals compared to subsurface water (Pattenden et al., 1981; Kocan et al., 1987). The enrichment ratios of the microlayer concentration (MLC) to the subsurface concentration (SSC) varied largely and were related to water exchange, tide, current, etc. Some toxic trace metals (Cu, Pb) and microorganic pollutants can be highly enriched in the surface microlayer by as much as 1000 times the bulkwater values (Pattenden et al., 1981). Microlayer concentrations of OT compounds were higher than in the subsurface waters at all the sampling stations. Maximum concentrations occurred at S5, with a higher proportion of TBT (70.7%), the inlet to the western harbor with poor water exchange, and near the shipyard. Mean enhancement ratios of MLC to SSC were 2.5–10 for ∑OTs and 2.4–4.8 for MBT. Cleary and Stebbing (1987) studied OT compounds in the surface microlayer and subsurface waters in the southwest of England and found that the enhancement ratios of OTs and TBT were 9.8 and 6.3, respectively. Clearly, microlayer contamination is a potential threat to microalgae and the larval stages of fish, which live in the microlayer.

### 3.3. Partitioning of organotin compounds in water/SPM and water/sediment

The physical and chemical properties of OT compounds determine their environmental behavior in the coastal environment. It has been found that the partitioning constant  $D_{oc}$  between seawater and sediments ( $D_{oc} = OT \text{ Conc. in sediment} / OT \text{ Conc. in seawater}$ ), which is in the order TBT ≥ DBT ≥ MBT, is controlled by the particulate organic carbon, lipid content, etc (Berg et al., 2001). Therefore, mono-tin compounds tend to exist in the dissolved phase of water. TBT and TPhT compounds were more hydrophobic

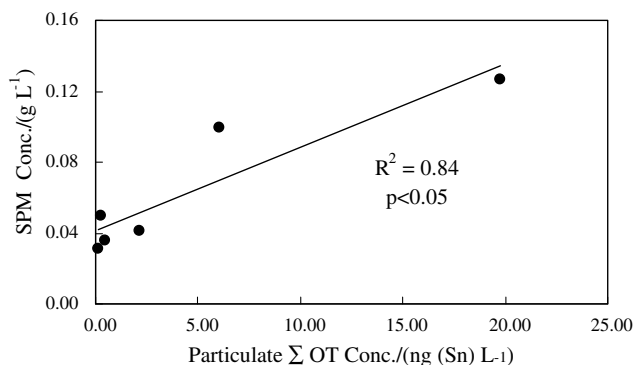


Fig. 2. Relationship between SPM concentration and particulate organotin compounds in the seawater of Xiamen area.

and easily adsorbed on the surface of particles. Although particulate  $\Sigma$ OT concentrations were lower than dissolved  $\Sigma$ OT concentrations, particulate  $\Sigma$ OT and SPM concentration showed a significantly positive linearly relationship ( $R^2 = 0.84$ ,  $p < 0.05$ , Fig. 2) in the Xiamen sea area, which implied that OT tends mainly to adsorb onto clay and biological particles of SPM.

OT concentrations in sediments and overlying waters from the same site usually show a significant relationship, for example in Aburatsubo Bay, Japan, and Mormugao Harbor, India (Bhosle et al., 2004). Because of high concentrations of OT accumulated in the surface sediment, OT could be released from particles to the overlying water. But in this study, we did not find this relationship in the Xiamen sea area ( $t$ -test,  $P > 0.05$ ). Similar results are found in seawater and sediments in 21 Taiwan harbors (across the Taiwan Strait from Xiamen) between 2001 and 2004 (Lee et al., 2006), which indicate that TBT is not transported from the sediment to the overlying water. Lee assumes that this spatial TBT distribution pattern may indicate the influence of in situ bacterial decomposition, tides and current movements in the area.

#### 3.4. Historical pollution of organotin compounds in sediment cores

The half life of TBT in sediment was long to several years (Stewart and Thompson, 1997). Sediment cores can be used to investigate temporal contamination trends in the past. In this study, S3, S4, S6 sediment cores were collected to trace the history of TBT contamination in Xiamen western harbor. Based on  $^{210}\text{Pb}$  dating, the sediment deposition rates in stations S3, S4 and S6 are 4.2 cm/a, 2.8 cm/a and 2.3 cm/a, respectively (Zeng et al., 1991).

As shown in Fig. 3, vertical distribution of TBT and  $\Sigma$ OTs varied according to the depth. The maximum concentration occurred at depths of 21–24 cm, 15–18 cm and 15–18 cm for the S3, S4 and S6 sediment cores, respectively, which are the layers tested in 2000 (Fig. 3). These results indicate that a large input of TBT into coastal environment of Xiamen occurred during 2000, which is related to the impact of diffuse OT compounds from the heaviest shipping activities for the construction of Haicang Bridge from June 1997 to December 1999. Also, at station S06, there has been increasing concentration of TBT as well as OTs at surface layer on the year around 2005, the probably reason may be related to the heavier shipping activities for withdraw the mariculture in the inlet harbor for environment integrate management by Xiamen government during 2003 and 2004.

Yuan and Zhong (2001) investigated the OT compounds in the surface sediments of Xiamen western harbor in 1999. The results for MBT, DBT and TBT near station S04 are 0.52, 0.74 and 4.3 ng(Sn)  $\text{g}^{-1}$ , which is similar to our measured data at the same station (1.2, 0.76 and 3.3 ng(Sn)  $\text{g}^{-1}$ , respectively). Comparing these results indicated that TBT had been degraded to DBT and MBT, and OTs were mainly from TBT and its degradation products after 7 years.

In surface sediment and sediment cores, MBT was dominant amongst the total OT compounds and TBT had a declining trend with depth in Xiamen harbor, as in Chinhae Bay, Korea (Hwang et al., 1999) and Malaysian marine environments (Sudaryanto et al., 2004), thus indicating that TBT is degraded during deposition and/or in the sediment. The degradation rate of TBT in the sediments is usually faster than that of its degradation products DBT and MBT, which is related to the sedimentation rate, bacterial activities and the input of TBT. Compared with previous results at the west coast of India (1.4–2800 ng(Sn)  $\text{g}^{-1}$  (dw) in the sediment, Bhosle et al., 2004) and Chinhae Bay, Korea (22–254 ng(Sn)  $\text{g}^{-1}$ , MBT was dominant in the sediment, Hwang et al., 1999), the Xiamen sea area was lightly contaminated by OTs. The amount and pattern of OTs in the sediment cores also indicated a lower contamination and a homogenous distribution of these compounds in Xiamen's western harbor.

#### 4. Conclusion

MBT was the dominant OT in most seawater and sediment samples, indicating that TBT has been degraded during input and deposition, and that there is a lower contamination by OTs in the coastal environment of Xiamen. The high concentration of OTs and a larger proportion of TBT than its degradation products occurred at the inlet of the harbor indicating fresh input in the Xiamen sea area.

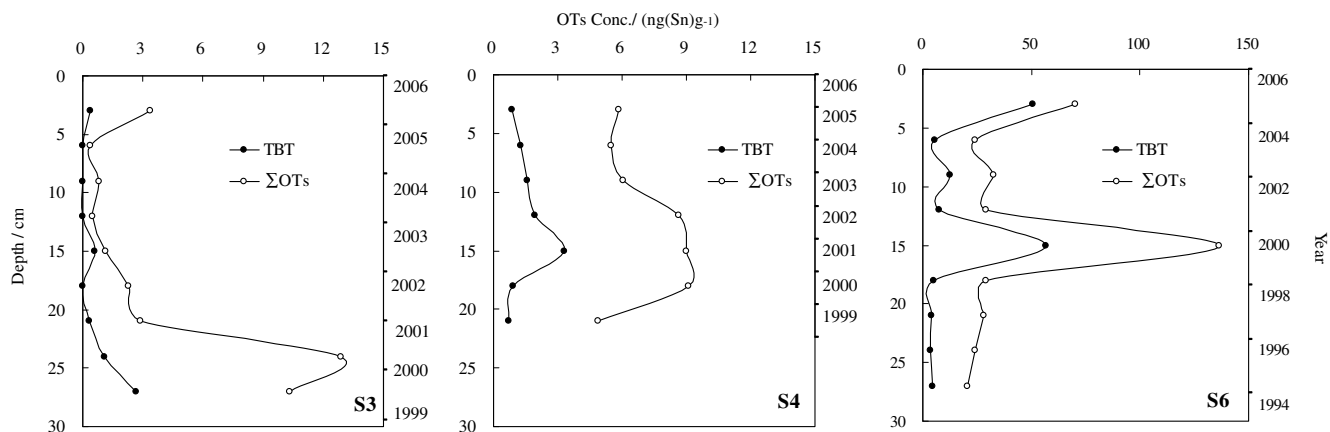


Fig. 3. Vertical distribution of TBT and total organotin compounds in sediment cores from Xiamen western harbor.

Compared with other harbors and bays in the world, contamination in the coastal waters of Xiamen was lower. The data in this paper also demonstrated that OTs can be enriched in the microlayer water and that the potential toxicity of these pollutants to larval organisms should be of some concern.

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