



Distribution of Butyltins in Sediments of the Kaohsiung Ocean Disposal Site

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ABSTRACT

The distribution of butyltin (BT) compounds in sediments of the Kaohsiung Ocean Disposal Site (KODS) was investigated in this study. The sediment samples which collected from nine disposed stations and two reference stations in the KODS in 2009 and 2010 were analyzed for monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT). Experimental readings showed that in 2009 the concentration of total butyltins (Σ BTs) varied from 0.3 to 1.5 ng Sn/g dw for disposed stations, and 2.6 ng Sn/g dw only reference stations, for which most of BTs came from TBT. Whereas 2010 the BTs concentration varied from 0.3 to 69.3 ng Sn/g dw for disposed stations, and 0.4 to 2.2 ng Sn/g dw for reference stations, for which most of BTs came from TBT. Referring to the TBT-contaminated sediment classification, the sediment samples collected from disposed stations in 2010 could be classified as moderately to highly contaminated, and disposal site in 2009 could be classified as uncontaminated. On the other hand, when referring to the Oslo and Paris (OSPAR) biological effects of assessment, the TBT concentration within the sediment samples of disposed stations in 2010 might affect benthos but not necessarily responded for females to be sterile, and in 2009 of the biological response caused by TBT concentrations was below the environmental assessment criteria for the disposal site.

Keywords: Dibutyltin (DBT); Monobutyltin (MBT); Ocean disposal; Tributyltin (TBT)

1. INTRODUCTION

The market of butyltin compounds (BTs) which were particularly used as thermal and UV stabilizers for polyvinyl chloride (PVC) began to expand in 1940s for use in plastic industry. And the tributyltin (TBT) was used as antifouling paints for boat due to its biocidal properties after 1960s (Hoch, 2001). However, all those various applications of organotin compounds may cause a direct and/or indirect input for the aquatic environment. It was estimated that about 30% of organotins would eventually enter the aquatic

environment, especially in harbors with heavy shipping traffic around the world (Mzoughi et al., 2005; Sun et al., 1996).

TBT are known as endocrine disruptor chemicals, and even at very low concentrations (i.e., the low nanogram per liter range) it can cause detrimental effects on the organisms in aquatic systems, which includes gastropod imposex, oyster malformation, and mussel larvae mortality. Consequently, phased out TBT as biocide in antifouling paints, following a recommendation by the International Maritime Organization (Champ, 2000; Hoch, 2001; Michaud and Pelletier, 2006), and several countries have promulgated laws to control the usage of TBT. In Taiwan, the

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ban on TBT-containing antifouling paints on ships of less than 25 m has been effective since 2003, and the ban was applied to all ships 2008. Although, these regulations have enabled a decrease in TBT concentrations in the water column (Omae, 2003; Regoli et al., 2001), TBT has still been detected in water, sediment, and organism from many areas (Díez et al., 2002; Regoli et al., 2001; Verslycke et al., 2005).

Kaohsiung Harbor is situated at the southwestern coast of Taiwan, and faces the key trade waterway running through the Taiwan Strait and Bashi Channel. The harbor has more than 34,388 inbound and outbound vessels every year between 1993 and 2010. It is the largest international sea port in Taiwan (KHB, 2011). Previous studies pointed out that the fishing port and the shipyards within the region of sediment accumulated high concentrations of total butyltin (Σ BTs) (1.69 to 14373 ng Sn/g dry weight), for which may be affected by the release of TBT in hull from the ship dock and the repair/construction of vessels (Chen et al., 2010; Lee and Wang, 2003). In addition to the pollutants from ships, the river estuary injection, such as the Love River in Kaohsiung Harbor contributed dibutyltin (DBT), is another source of BTs (Chen et al., 2010).

In order to maintain proper depth, to facilitate ships incoming and outgoing, Kaohsiung Harbor needs for regular port sediments dredging. Then the dredged sediments will be transported to the Kaohsiung Ocean Disposal Site (KODS) for disposal by the specification of ocean disposal method. The KODS was the only approved operating ocean disposal site in Taiwan. It has been disposed of about 2.1 million tons of the harbor sediments since 2004 (Dong et al., 2010).

Worldwide, if harbor sediments are contaminated with persistent organic pollutants such as TBT, it would pose a hazard for the receiving marine systems (Stronkhorst and

Hattum, 2003). Thus, has the KODS once been impact of ocean disposal action; it may cause a negative affection upon environmental quality. The objectives of this study are to investigate the distribution of BT compounds in sediments from the KODS. This study is the first report on BT compounds contaminations in the KODS of Taiwan.

2. MATERIALS AND METHODS

2.1 Sampling Strategy

The KODS was located 12 to 15 nautical miles from the coast with E120°03.59", N22°27.57" as the center, side length of 6 km square area, and the water depth from 500 to 700 meters. Eleven sampling stations selected in this study included two outer disposal site stations (S10, S11 reference stations) and nine disposal stations (S01, S02, S03, S04 were disposal site vertex angle, S05 was disposal site center and S06, S07, S08, S09 were disposal area centers, Fig. 1).

2.2 Sampling Collection

The Ocean Researcher III was hired to collect the sediment samples from various locations in the KODS during March, May, August and October in 2009 and 2010. About 3 kg of sediments were collected with an SIHPEK grab sampler. Immediately after collection, the samples were transferred into polyethylene bags and kept in an ice box and then transported to the laboratory for analysis. In the laboratory, the samples were kept at $20 \pm 2^\circ\text{C}$ until further processing and analysis.

2.3 Sample Preparation Analysis

Particle size was determined with a particle size counter (Coulter LS 100, Particle Size Analyzer). Wet sediment samples were placed in an oven at 105°C and heated to a constant

weight. Then, the water content of sediment samples was calculated by the weight difference before and after heating. The dry sediment samples were further heated at 550°C overnight, and the weight difference with respect to dry weight (dw) was determined as the organic matter (OM) content (APHA, 2005).

BT compounds were extracted from the sediment samples following the Draft DIN 38407-13 (German standard method 1999). Briefly, 3 g of freeze-dried ($-80 \pm 2^\circ\text{C}$) sediment samples (dry mass) were put into clean brown glass jar, then 10 mL of acetate buffer solution (pH 4.5), 0.2 mL of 10% NaBEt₄ derivating agent, and 500 ng of TePeT as internal standard were added. A blank was prepared following the same procedure without sediment samples. A standard mixture was prepared by adding to buffer with acetate (pH 4.5). All samples were vortexed for 10 min. Then, 5 mL of 0.02% tropolone-hexane was added to the glass jar, and the mixture was ultrasonic for 30 min to extract BT compounds. The glass jar was then centrifuged for 5 min at 2,000 rpm. Hexane layer containing the derivatized compounds was siphoned out with a Pasteur pipette, and the buffer layer was re-extracted twice with 0.02% tropone-hexane. Hexane layer containing the BTs were pooled together. Activated copper was added into hexane extract for desulfurization. Extract was concentrated to 0.5 mL using a gentle stream of nitrogen, and then analyzed by gas chromatography (GC).

An Agilent 4890D Series GC equipped with a HP-5 capillary column (30 m \times 0.535 mm \times 1.5 μm), a Flame photometric detector (FPD), and a tin-specific filter (610 nm) were used to separate and quantify the BTs. The column temperature was initially held at 40°C for 5 min, raised to 250°C at the rate of 15°C/min, and held at this temperature for 5 min. Samples were injected in the split less mode

at injection temperature of 250°C. Detector temperature was kept as 250°C. Nitrogen was used as a carrier gas (6 mL/min). Hydrogen and air flows were maintained at 75 and 100 mL/min, respectively.

In the present study, all BTs concentrations are reported as nanogram Sn per gram dry weight.

2.4 Quality Control

Five-point calibration curve (0.1, 0.3, 0.5, 0.7, and 0.9 ng Sn/g), procedural blank, and check standard were carried out for every set of samples. The linear regression coefficient of calibration curve showed an acceptable linear correlation ($r^2 > 0.995$), the procedural blanks value were always smaller than the detection limit, and the recoveries of check standard ranged from 85% to 100%. The limit of detection of the analytical procedure was estimated from 3 times the standard deviation from multiple duplicate ($n=7$) analysis BTs of 0.5 $\mu\text{g/L}$ and the amount of sample extracted. The detection limits of BTs were monobutyltin (MBT) (0.59), DBT (0.52), and TBT (0.31) for sediment (ng Sn/g dw).

BCR Reference Matter NO 424 (RM 424) (Industrial harbor sediment) from Commission of the European Communities, certified for TBT (20 $\mu\text{g/kg}$) concentrations was used. The measured value for TBT in RM 424 was 18.7 ± 0.5 $\mu\text{g/kg}$ ($n=3$).

3. RESULTS AND DISCUSSION

3.1 Grain Sizes and OM Contents of Sediments

Table 1 lists the grain sizes of sediment samples in the KODS at 2009 and 2010. The grain sizes in all sediment samples were mainly silt (2-63 μm) about 10.8% to 83.8%, secondly clay (<2 μm) and sand (>63 μm), 2.6% to 22.5% and 0.0% to 86.5%. The grain

sizes distribution showed that the sediments in the KODS were composed by fine grained dominated (Fig. 2). However, the standard deviations of grain sizes for every single disposed station varied slightly from time to time. This could be seen especially in stations S01, S05, S06, and S09. On the other hand, the observation values of OM contents in all

sediment samples from the KODS at 2010 ranged from 1.1% to 6.7%, which were slightly higher than those ranging 0.8 to 6.2% at 2009 (Fig. 3). All observed data showed that all stations in the KODS at 2009 and 2010 varied from time to time, and it may be subjected to the disposal impact of harbor dredged sediments as we can tell.

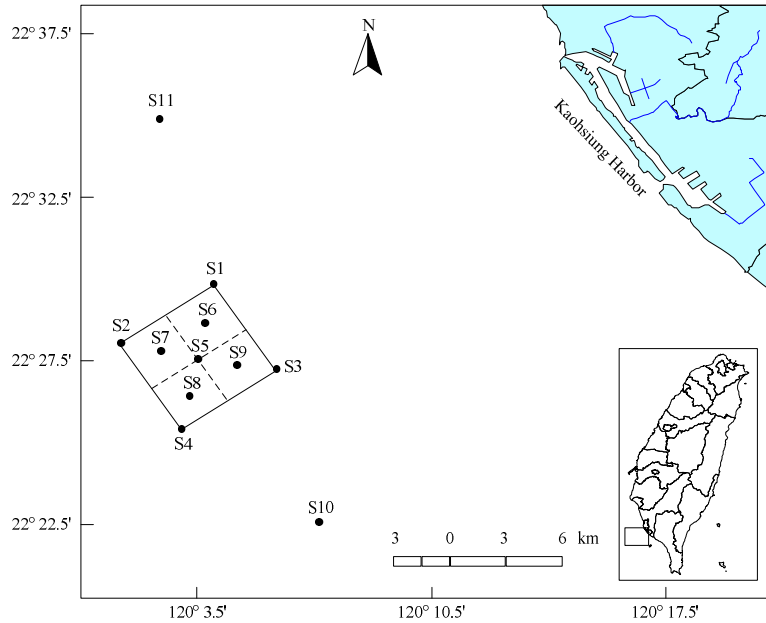


Figure 1 Study area and sampling sites

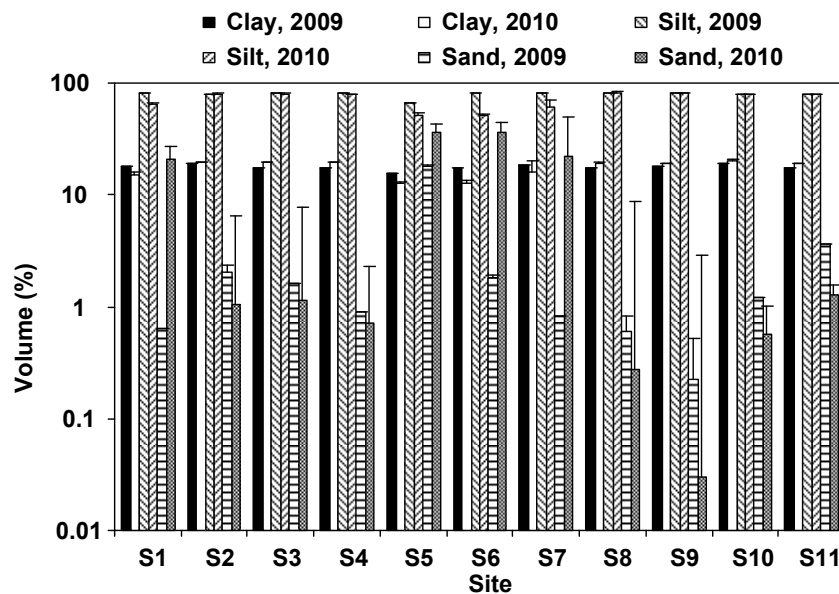


Figure 2 Distribution of grain sizes in sediments of the KODS (n=4)

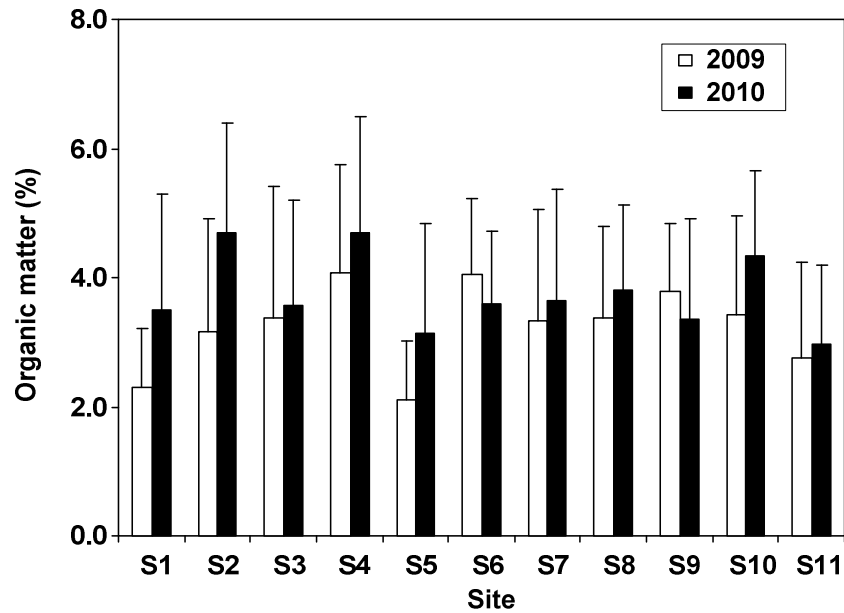


Figure 3 Distribution of organic matter contents in sediments of the KODS (n=4)

Table 1 Grain sizes and OM content in the sediments of the KODS at 2009 and 2010

Site	Clay (<2 μ m) (%)				Silt (2-63 μ m) (%)				Sand (>63 μ m) (%)				OM (%)			
	Mar.	May	Aug.	Oct.	Mar.	May	Aug.	Oct.	Mar.	May	Aug.	Oct.	Mar.	May	Aug.	Oct.
2009																
S1	16.7	17.4	18.0	19.1	83.3	82.5	81.9	78.6	0.0	0.1	0.1	2.3	2.22	2.79	1.08	3.13
S2	19.5	16.8	20.9	20.0	80.0	82.0	75.9	75.9	0.6	1.2	3.2	3.2	2.73	3.01	1.39	5.56
S3	17.8	16.1	18.7	18.2	81.7	80.0	80.7	80.5	0.5	3.9	0.7	1.3	2.54	3.61	1.30	6.09
S4	17.3	17.2	18.4	17.1	82.1	80.6	81.1	82.5	0.6	2.2	0.4	0.5	3.42	4.37	2.24	6.24
S5	18.4	17.7	20.4	5.7	80.8	81.8	78.4	23.8	0.8	0.5	1.1	70.5	2.27	2.80	0.78	2.57
S6	17.9	16.8	16.9	18.1	81.4	82.3	82.4	76.9	0.7	0.9	0.7	5.0	2.85	3.40	4.50	5.48
S7	19.5	16.6	19.0	18.5	79.9	82.0	80.4	80.7	0.6	1.4	0.6	0.8	2.44	3.57	1.73	5.63
S8	17.0	16.7	18.0	18.1	82.9	83.3	82.0	79.6	0.1	0.0	0.0	2.3	2.54	3.71	2.06	5.21
S9	17.6	17.9	17.4	19.8	82.4	82.1	82.6	79.4	0.0	0.0	0.0	0.9	2.46	3.41	4.37	4.85
S10	18.6	17.7	18.4	21.5	80.4	80.1	80.8	77.7	1.0	2.2	0.9	0.8	3.29	3.18	1.73	5.48
S11	17.1	16.0	18.4	18.1	72.2	82.6	80.4	80.7	10.7	1.4	1.2	1.2	1.48	3.24	1.68	4.65
2010																
S1	18.5	21.0	18.4	3.4	81.5	79.0	81.6	13.9	0.0	0.0	0.0	82.7	4.81	5.13	1.29	2.70
S2	19.0	20.7	18.5	19.3	80.5	78.5	81.5	77.8	0.5	0.8	0.0	2.8	4.78	6.01	2.26	5.69
S3	19.5	19.2	20.7	19.6	80.0	80.3	79.3	76.8	0.5	0.5	0.0	3.6	3.05	5.04	1.53	4.68
S4	22.1	19.4	17.9	18.6	77.9	80.6	81.8	78.9	0.0	0.0	0.4	2.5	4.42	6.72	2.40	5.24
S5	20.3	18.8	4.2	6.9	79.7	80.5	17.4	27.4	0.0	0.7	78.5	65.7	2.72	5.18	1.09	3.54
S6	3.5	20.2	18.8	7.8	14.2	79.4	79.6	30.0	82.3	0.5	1.6	62.2	2.36	5.06	3.32	3.65
S7	19.0	20.8	22.5	2.6	80.3	78.6	77.5	10.8	0.7	0.6	0.0	86.5	4.36	5.66	1.77	2.81
S8	19.1	19.0	19.3	19.2	80.9	79.9	80.7	80.9	0.0	1.1	0.0	0.0	3.90	4.43	1.92	4.95
S9	18.9	19.4	20.1	18.4	81.1	80.6	80.0	81.5	0.0	0.0	0.0	0.1	3.55	4.02	1.14	4.72
S10	20.4	20.1	20.2	21.3	79.1	79.2	79.1	78.2	0.5	0.6	0.6	0.5	4.07	5.55	2.55	5.13
S11	20.7	18.8	18.3	19.6	78.6	80.2	80.0	78.7	0.7	1.0	1.8	1.7	3.11	3.69	1.24	3.88

Table 2 Concentration of butyltin compounds in the sediments of the KODS at 2009 and 2010

Site	MBT (ng Sn/g dw)				DBT (ng Sn/g dw)				TBT (ng Sn/g dw)				BTs (ng Sn/g dw) ^a			
	Mar	May	Aug.	Oct.	Mar.	May	Aug.	Oct.	Mar.	May	Aug.	Oct.	Mar.	May	Aug.	Oct.
2009																
S1	0.63	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	<0.3 1	<0.3 1	1.46	<1.4 2	<1.4 2	<1.4 2
S2	<0.59	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	1.02	<0.3 1	<0.3 1	<1.4 2	2.13	<1.4 2	<1.4 2
S3	<0.59	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	<0.3 1	<0.3 1	<1.4 2	<1.4 2	<1.4 2	<1.4 2
S4	<0.59	<0.5 9	0.76	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	<0.3 1	<0.3 1	<1.4 2	<1.4 2	1.59	<1.4 2
S5	<0.59	<0.5 9	<0.5 9	0.66	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	0.57	<0.3 1	<0.3 1	<1.4 2	1.68	<1.4 2	1.49
S6	<0.59	<0.5 9	0.60	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	0.51	<0.3 1	<1.4 2	<1.4 2	1.63	<1.4 2
S7	<0.59	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	<0.3 1	<0.3 1	<1.4 2	<1.4 2	<1.4 2	<1.4 2
S8	<0.59	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	0.80	<0.3 1	<1.4 2	<1.4 2	1.91	<1.4 2
S9	<0.59	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	0.90	<0.5 2	<0.3 1	0.92	0.39	<0.3 1	<1.4 2	2.03	1.88	<1.4 2
S10	<0.59	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	<0.3 1	<0.3 1	<1.4 2	<1.4 2	<1.4 2	<1.4 2
S11	<0.59	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	<0.3 1	<0.3 1	<0.3 1	<0.3 1	<1.4 2	<1.4 2	<1.4 2	<1.4 2
2010																
S1	1.65	<0.5 9	<0.5 9	1.99	6.40	<0.5 2	2.50	1.10	15.9	<0.3 1	4.82	10.1	24.0	<1.4 2	7.91	13.2
S2	<0.59	<0.5 9	0.82	<0.5 9	1.47	<0.5 2	6.28	<0.5 2	4.56	<0.3 1	11.8	<0.3 1	6.62	<1.4 2	18.9	<1.4 2
S3	<0.59	<0.5 9	<0.5 9	<0.5 9	5.08	<0.5 2	3.83	<0.5 2	12.8	<0.3 1	10.3	<0.3 1	18.5	<1.4 2	14.7	1.42
S4	0.80	<0.5 9	<0.5 9	<0.5 9	1.01	<0.5 2	1.67	<0.5 2	3.57	<0.3 1	3.17	1.05	5.38	<1.4 2	5.43	2.16
S5	1.16	<0.5 9	1.81	<0.5 9	5.33	<0.5 2	7.25	<0.5 2	13.7	0.33	12.0	2.43	20.2	1.44	21.1	3.54
S6	0.71	<0.5 9	1.07	2.87	2.56	<0.5 2	6.19	1.98	12.5	<0.3 1	16.5	5.77	15.8	<1.4 2	23.8	10.6
S7	8.24	<0.5 9	<0.5 9	0.69	20.2	<0.5 2	3.03	<0.5 2	58.9	<0.3 1	10.3	1.56	87.3	<1.4 2	13.9	2.77
S8	1.21	<0.5 9	1.49	1.25	3.44	<0.5 2	6.66	1.30	10.3	<0.3 1	11.3	20.8	15.0	<1.4 2	19.5	23.4
S9	0.85	<0.5 9	<0.5 9	0.84	2.24	<0.5 2	2.37	0.87	9.06	2.28	7.03	5.80	12.2	3.39	9.99	7.51
S10	0.97	<0.5 9	<0.5 9	<0.5 9	<0.5 2	<0.5 2	<0.5 2	<0.5 2	0.71	<0.3 1	1.23	<0.3 1	2.20	<1.4 2	2.34	<1.4 2
S11	<0.59	<0.5 9	<0.5 9	<0.5 9	1.27	<0.5 2	<0.5 2	<0.5 2	0.96	<0.3 1	0.52	<0.3 1	2.82	<1.4 2	1.63	<1.4 2

^a BTs = MBT + DBT + TBT

3.2 Distribution of Butyltin

Table 2 and Fig. 4 showed BTs concentrations of sediment samples in the KODS at 2009 and 2010, and Fig. 5 showed Σ BTs average concentration of sediment samples in the KODS at 2009 and 2010. The concentration of monobutyltin (MBT) varied from <0.59 to 8.24 ng Sn/g dw, DBT varied from <0.52 to 20.2 ng Sn/g dw, TBT varied from <0.31 to 58.9 ng Sn/g dw, and Σ BTs varied from <1.42 to 87.3 ng Sn/g dw in all sediment samples from the KODS at 2009 and 2010. At 2009, the concentrations of MBT varied from 0.60 to 0.76 ng Sn/g dw were detected at stations S1, S4, S5, and S6, DBT was 0.9 ng Sn/g dw at station S1, TBT varied from 0.51 to 0.92 ng Sn/g dw were detected at stations S2, S5, S6, S8 and S9, and Σ BTs varied from 0.3 to 2.6 ng Sn/g dw in all sediment samples. The concentrations of Σ BTs varied from <1.42 to 2.13 ng Sn/g dw in sediment samples from disposal site boundary (S1 to S4) and disposal site inner (S5 to S9), for which most of Σ BTs came from TBT, and Σ BTs was <1.42 ng Sn/g dw in sediment samples from reference stations (S10 and S11). The concentrations of Σ BTs in sediment samples from the KODS at 2010 were higher than those at 2009. The concentrations of MBT varied from 0.69 to 8.24 ng Sn/g dw were detected at stations S1, S2, and S4 to S10, DBT varied from 1.01 to 7.25 ng Sn/g dw were detected at stations S1 to S09, and S11, TBT varied from 0.33 to 58.9 ng Sn/g dw were detected at S1 to S11 stations, and Σ BTs varied from 0.3 to 69.3 ng Sn/g dw in all sediment samples. The concentrations of Σ BTs varied from <1.42 to 23.9 ng Sn/g dw in sediment samples from disposal site boundary, Σ BTs varied from <1.42 to 87.3 ng Sn/g dw in sediment samples from disposal site inner, and Σ BTs varied from <1.42 to 2.82 ng Sn/g dw in sediment samples from reference stations, for which most of BTs came from TBT.

The variances of Σ BTs in disposal site inner were slightly higher than those of the ocean disposal boundary, while the variances of stations were among the lowest. It was probably because of that the KODS at 2009 was mainly exposed to low concentrations of BTs in dredged sediments that came from the harbors, but at 2010, it was mainly high concentrations of BT in dredged sediments that came from the shipyards. It indicated that BT-containing dredged sediments, which were disposed by ocean disposal behavior, may directly affect the BT-containing in sediments of the KODS.

3.3 TBT-Contaminated Sediments Classification In The KODS

Dowson et al. (1993) suggested a classification, which base on the concentrations of TBT in sediments, into five categories as uncontaminated (<1.2 ng Sn/g), lightly contaminated (1.2–8.2 ng Sn/g), moderately contaminated (8.2–41 ng Sn/g), highly contaminated (41–205 ng Sn/g), and grossly contaminated (>205 ng Sn/g). Table 3 showed the classification of TBT-contaminated sediments in the KODS at 2009 and 2010. The site was classified by its position into three areas: disposal site boundary (S1 to S4), disposal site inner (S5 to S9), and reference stations (S10 and S11). Referring to the study of Dowson et al. (1993), the concentrations of TBT varied from <0.31 to 1.02 ng Sn/g dw in disposal site boundary and disposal site inner (S5 to S9). Moreover, TBT in reference stations at 2009 were below the limit of detection (LOD), and could be classified as uncontaminated. At 2010, the concentrations of TBT varied from <0.31 to 15.9 ng Sn/g dw in disposal site boundary, and could be classified as uncontaminated to moderately contaminated. The TBT concentrations varied from <0.31 to 58.9 ng Sn/g dw in disposal site inner, and could be classified as uncontaminated to highly

contaminated. Furthermore, the TBT concentrations varied from <math><0.31</math> to 1.23 ng Sn/g dw in reference stations, and could be classified as uncontaminated to lightly contaminated.

The results of study showed that the sediment samples of disposal site inner at 2010 could be highly contaminated, in which the disposal of dredged sediments from fishing

port may be directly or indirectly caused increasing of TBT-contamination. The sediment samples of disposal site boundary at 2010 could be moderately contaminated, in which the TBT-contamination may be affected by tide, diffusion currents, or the balance of the KODS.

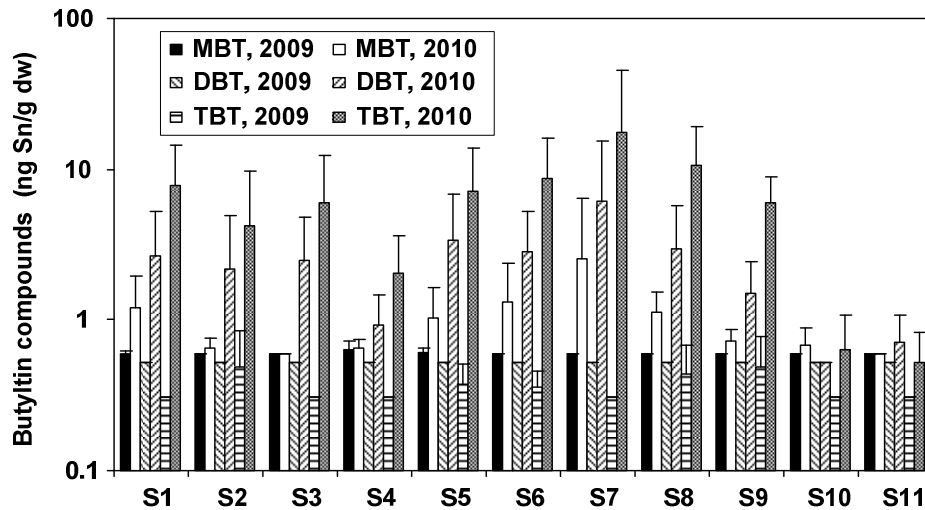


Figure 4 Distribution of butylin compounds in sediments of the KODS (n=4)

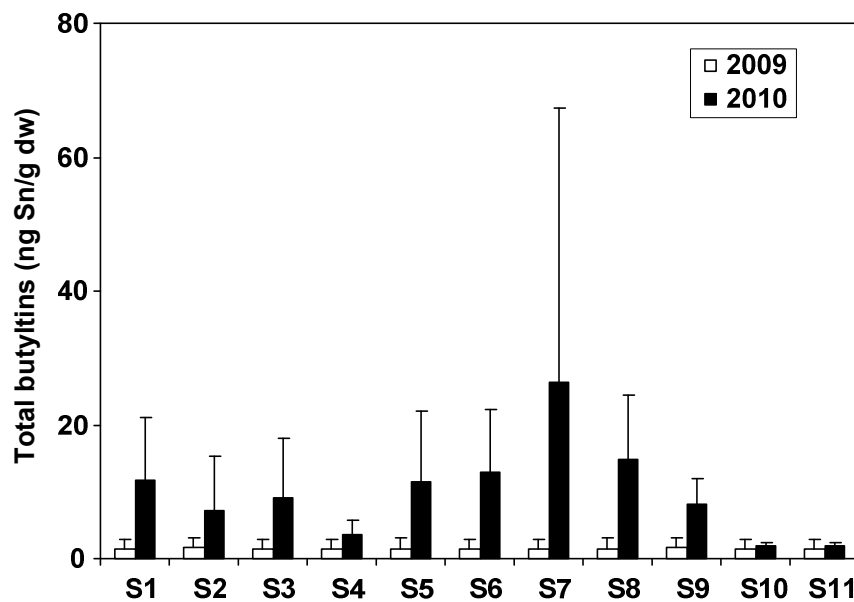


Figure 5 Distribution of total butyltins contents in sediments of the KODS (n=4)

Table 3 Classification of TBT-contaminated sediments in the KODS at 2009 and 2010

TBT ^a	Classification ^b	Stations from the KODS	
		2009	2010
<1.2	Uncontaminated	Disposal site boundary, disposal site inner, and reference stations	Reference stations
1.2-8.2	Lightly contaminated		
8.2-41	Moderately contaminated		Disposal site boundary
41-205	Highly contaminated		Disposal site inner
>205	Grossly contaminated		

^a units: ng Sn/g dw.^b TBT-contaminated sediments classification (Dowson et al. 1993)**Table 4** Biological effects of assessment in the KODS at 2009 and 2010

TBT ^a	Classification ^b	Stations from the KODS	
		2009	2010
nd	A	Reference stations	
<2	B	Disposal site boundary and disposal site inner	Reference stations
2-50	C		Disposal site boundary
50-200	D		Disposal site inner
200-500	D		
>500	F		

^a units: ng Sn/g dw, ^b Biological effects of assessment (OSPAR 2009)

3.4 Biological Effects of Assessment in The KODS

Osla and Paris Commission (OSPAR 2009) by biological response of *Nucella lapillus* to TBT concentration in sediment was divided into six classes: Class A was close to zero effects (nd), Class B was response caused by TBT concentrations below the ecotoxicological assessment criteria (<2 ng Sn/g dw), Class C was response where females are not expected to be sterile (2–50 ng Sn/g dw), Class D was sterile females are present in the population, but reproductively capable females remain (50–200 ng Sn/g dw), Class E was populations are unable to reproduce (200–500 ng Sn/g dw), and Class F was populations of *Nucella* have expired (>500 ng Sn/g dw).

Table 4 showed biological effects of as-

essment in sediment samples from the KODS at 2009 and 2010. At 2009, the concentrations of TBT varied from <0.31 to 1.02 ng Sn/g dw in disposal site boundary and disposal site inner, and could be classified as biological effects of assessment was class A to B, and TBT below LOD in reference stations could be classified as class A. It indicated that at 2009, the concentrations of TBT in disposal site inner was not likely causing negative biological response onto *Nucella lapillus*. At 2010, the concentrations of TBT varied from <0.31 to 15.9 ng Sn/g dw in disposal site boundary, and could be classified as was class A to C, and it is showed the concentrations of TBT in disposal site boundary was likely causing biological response onto *Nucella lapillus*, but not expected to be sterile. Furthermore, the concentrations of TBT varied

from <0.31 to 58.9 ng Sn/g dw in disposal site inner could be classified as was class A to D, and it is showed the concentrations of TBT in disposal site inner was likely causing sterile females *Nucella lapillus* were present in the population, but reproductively capable females remain.

The results of study showed that at 2010, the disposal site inner for biological effects assessment was class D, due to the disposal of high concentrations TBT-containing dredged sediments from fishing port. Moreover, the TBT-containing dredged sediments diffusion would cause impaction onto marine organisms within the neighborhood.

CONCLUSIONS

TBT, DBT, and MBT were detected in sediment samples collected from the various locations of the KODS. The relative high levels of Σ TBs were recorded for sediment samples from disposal site inner. This suggests that these ocean disposal actions played important roles in the leaching of TBT-containing dredged sediments into the KODS. However, with the TBT-containing dredged sediments may be diluted or spread into the ocean, it may further severe impact to the ocean ecological within adjacent areas. The results of this study can be provided to the relevant agencies as a matter of reference for ocean disposal standards.

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