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Contamination and Bioaccumulation of Butyltin Compounds Inside Jeju Harbor of Jeju Island, Korea

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Abstract

Butyltin compounds in seawater, sediments and organisms inside Jeju Harbor of Jeju Island, Korea, were quantitatively determined to assess the extent of contamination and to evaluate the bioaccumulation in *Thais clavigera* (gastropod), *Liolophura japonica* and *Cellana nigrolineata*. In addition, imposex in *T. clavigera* was used to assess the sublethal effect of tributyltin compounds and its usage as a specific biomarker for these compounds was also studied. The main species in seawater was tributyltin (TBT) in March and June, monobutyltin (MBT) in August, but in sediments and organisms it was dibutyltin (DBT) and TBT, respectively, irrespective of survey time. TBT, the most toxic to aquatic organisms among BTs, was found at concentrations which were sufficient to have a serous effect on the sensitive organisms upon chronic exposure. The high correlations ($r>0.7$) between BTs indicated that DBT and MBT were mainly degraded from TBT based on antifouling paints and their sources were negligible. The sedimentary organic matters have little influence on the distribution of BTs in marine environment and the lipid content in *T. clavigera* showed a significant correlation with TBT concentrations. Measurement of imposex *T. clavigera* was expected to be a very helpful tool for preliminary survey of BTs prior to trace analysis of those.

Key Words : Tributyltin, Dibutyltin, Monobutyltin, Seawater, Sediment, Organism, Imposex, Jeju harbor

1. Introduction

Organotin compounds are one of the most widely used organometallic compounds. The properties of organotin compounds depend on the number and the types of the organic groups (R). R_2SnX_2 and R_3SnX are mainly used in industry and agriculture. R_2SnX_2 as dibutyltin and dioctyltin compounds is used in large amounts as catalysts and heat and light stabilizer in poly (vinyl chloride) processing. Most of R_3SnX compounds exhibit biocidal activity. Triphenyltin, tripropyltin, tricyclohexyltin compounds are used mainly as pesticides in agriculture. Tributyltin (TBT) compounds are used for the mildew-resistant finishing of textiles and wood preservation. In addition, they are used as biocidal additives in antifouling paints to prevent adherence of sedentary organisms to ship hull and other structural surfaces immersed in water.

Major pathway of organotins (OTs) observed in marine environment is via uses as antifouling agents. Sewage sludge through riverine discharge maybe partly accounts for the inputs of these compounds (Tolosa et al., 1992). OTs released in water undergo photolytic (Batley, 1996) and biotic (Lee, 1989) degradation processes in natural condition and are readily adsorbed to particulate matters or bioaccu-

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mulated due to hydrophobicity given by substituted hydrocarbon chain (Strang and Seligman, 1987). Degradation processes produce de-alkylated or de–arylated compounds as well as inorganic tin. OTs adsorbed to particulate matters may be removed from water column to benthic environment, resulting in increased sediment concentration. OTs penetrate biological membranes more readily than inorganic tin and are more likely to accumulate in lipid-rich tissues or organelles as they are more soluble than inorganic tin in lipids of biota (Han and Cooney, 1994).

The toxicity of OTs has been extensively studied. Among them, TBT compounds are highly toxic, i.e., they even below a ppb level, cause oyster shell anomalities and spat fall failure (Alzieu, 1991), reduced growth and viability of various larvae (Beaumont and Budd, 1984) and imposex (imposition of male sexual organs on female) on neogastropod (Bryan et al., 1986).

Bioaccmulation and toxicity of TBT compounds released to aquatic environment from antifouling paints, cause deleterious effects on non-target organisms via diffusion, together with prevention of sedentary organisms to ship hull etc.. Their adverse effects on non-target organisms bring about an artificial disturbance in aquatic ecosystem. Thus, many countries have taken diverse steps to regulate the use of TBT-based antifouling paints in order to protect aquatic ecosystem. France in 1982, UK in 1987, USA in 1988, Japan in 1990 and Sweden in 1992, prohibited their use on boats of less than 25 m in length (Huggett et al., 1992), but they are still being used on vessels over 25 m in length. In Korea the regulation on their use was not legislated by 1998.

The coasts of Jeju Island has a good environmental condition as a spawning and a habitat of fishes and shellfishes as cold and warm currents cross, and seaweeds and sucked rocks are luxuriant. But shell deformation was observed inside harbor of Jeju Island by Lee et al. (1997). Thus, an urgent and systematic study on TBT compounds released from antifouling paints due to ships etc., is necessary in order to protect and manage aquatic organisms.

In this study, the seawater, sediments and organisms were collected inside Jeju Harbor where a lot of steady shipping occurs, in order to investigate the contamination, behavior and effects on organisms of TBT compounds, as an aspect of basic study on those in the coasts of Jeju Island. From seawater and sediments, the concentrations of TBT and its degradation products (dibutyltin, DBT and monobutyltin, MBT), the correlations between butyltins (BTs), the correlations between BT concentrations and organic matter content and the partition coefficients of BTs, were investigated. From organisms, the concentrations of BTs, biological concentration factor (BCF), the correlations between BT concentrations and lipid content, and the occurrence of imposex, were investigated.

2. Materials and Methods

2.1. Chemicals

The standards [$BuSnCl_3$ (MBT-Cl_3), Bu_2SnCl_2 (DBT-Cl_2), Bu_3SnCl (TBT-Cl)], GC internal standard [Bu_4Sn (TeBT)], tropolone and Grignard reagent [HeMgBr (HMB)] were obtained from Aldrich Chem. Co. (USA). A surrogate standard [Pen_3SnCl (TpenT-Cl)] was obtained from Kanto Chem. Co. (Japan). n-hexane and CH_2Cl_2 are HPLC grade and were obtained from Fisher Chem. Co. (USA). The other reagents were of analytical grade.

2.2. Collection of samples

Fig. 1 shows the sampling stations. Jeju Harbor is located at north-central part of Jeju Island, Korea. Inside Jeju harbor, total water area and its depth are 7.094×10^6 m^2 and in the range of 1.5-14.5 m, respectively, and the sediments of mud-type at inner sides and shell or sand-type at outer sides are present.

Outside Jeju Harbor, rock masses are present in a wide range and sediments are not.

Polycarbonate containers, which were washed with laboratory detergent, leached with 10% HNO_3 and rinsed repeatedly with deionized and distilled water, were used for sample collection. Seawater and sediment samples were collected at 12 stations (station # 1-12) inside Jeju Harbor in March, June and August, 1998, considering a breakwater and mooring sites of ships. As a comparison, seawater samples were collected at 2 stations (station # 13 and 14) outside Jeju Harbor. Five liter of seawater samples were collected at 0.3 m depth below surface in order to avoid surface microlayer films. Sediment samples were collected using van Veen grab. Organism samples (*Thais clavigera*, *Liolophura japonica* and *Cellana nigrolineata*) were collected from an intertidal zone inside Jeju harbor.

All the samples were immediately frozen after collection by dry ice in the field and transferred to the laboratory. On return to the laboratory, seawater and sediment samples were immediately frozen (-70°C). For organism samples, after shell length was measured, shells were removed and frozen (-70°C). Prior to analysis, the samples were thawed at room temperature or by gentle warming (40°C), but were not allowed to exceed room temperature and were analyzed still cool.

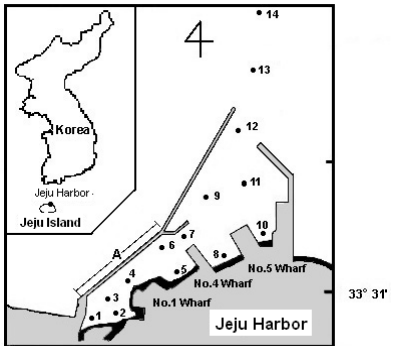

Fig. 1. Map showing sampling stations in Jeju Harbor (■:Mooring Site).

2.3. Determination of BTs

The method used for the determination of BTs is a modification of Stallard et al. (1989). One liter of unfiltered seawater sample was introduced into 2 L separatory funnel and adjusted to pH 2-3 with HCl. TpenT-Cl as a surrogate standard and 20 mL of 0.1% tropolone-CH_2Cl_2 mixture were added. The solution was allowed to stand for 5 min after being shaken manually for 3 min and on a reciprocating shaker for 10 min. The organic layer was separated into a 250 mL receiving flask. The other 4 L of seawater sample was extracted in the same way. The combined organic layer in the receiving flask was concentrated to 2 mL using a rotary evaporator, transferred to a 15 mL glass centrifuge tube, and concentrated to about 25 μL under a gentle stream of nitrogen. Then the samples were resuspended in 2 mL n-hexane and derivatized with 250 μL of 2 M HMB for 20 min. The remaining HMB was decomposed with 4 mL of 0.4 N H_2SO_4. The organic layer was separated by centrifugation and cleaned up on 2 g of activated florisil column. During the clean-up, the butyltin compounds were eluted with n-hexane. The cleaned extracts were concentrated again and spiked with TeBT as GC internal standard, and then analyzed by gas chromatograph (GC) - flame photometric detector (FPD) system.

Five gram of sediment sample (which was air-dried and ground) and TpenT-Cl as a surrogate standard were added to 50 mL polypropylene centrifuge tube. For digestion, the sample was mixed with 10 mL of HCl (1:1) and allowed to stand for 30 min. The digested sample was extracted by shaking for 3 hr with 20 mL of 0.1% tropolone-CH_2Cl_2 mixture. After centrifugation of the mixture, 2 mL of organic layer was transferred to a 15 mL glass centrifuge tube and concentrated to about 25 μL under a gentle stream of nitrogen. Then the subsequent procedure was the same as that for seawater analysis.

Organism sample was completely dried by a freeze dryer and homogenized with a Tekmar tissumizer. One gram of dry weight was transferred to a 50 mL polypropylene centrifuge tube and the subsequent procedure was the same as that for sediment analysis.

To remove carbonate from sediment, 1 N HCl was added to air-dried and ground sediment and they were completely dried at 60°C. Organic carbon content was determined using a CHN analyzer (Leuco CHN-900) which was calibrated with a potassium biphthalate.

Ten milliliter of organic layer extracted with 20 mL of 0.1% tropolone-CH_2Cl_2 mixture according to the procedure of BTs analysis in organism was transferred to a pre-weighed aluminum foil (W_1), dried for 48 hr in the air, and the re-weighed (W_2). The difference between W_1 and W_2 was calculated as lipid content.

After shell length of *T. clavigera* was measured to the nearest 0.01 mm using a vernier calipers, the shell was cracked and the tissues were separated. *T. clavigera* was sexed by appearance of a predominant female-ingesting gland (Horiguchi et al., 1994). The penis length of *T. clavigera* was measured to 0.01 mm using ImagePro image analyzer®. Two indices were used to assess the degree of imposex for *T. clavigera* collected in May, July and August, 1998: a relative penis length index (RPLI) was calculated as [(mean length of female penis)/(mean length of male penis) x 100]; a relative penis size index (RPSI) was calculated as [(mean length of female penis)^3/(mean length of male penis)^3 x 100].

3. Results and Discussion

Fig. 2 shows the distributions of BTs in unfiltered surface seawater from Jeju Harbor in 1998. BTs were detected in all seawater samples. The concentrations of TBT, DBT and MBT during all the survey times were in the range of 2.8-40.9 ng/L (mean 13.4 ng/L), 0.4-26.2 ng/L (mean 5.5 ng/L) and 1.5-54.0 ng/L (mean 12.6 ng/L) inside Harbor, 1.2-10.2 ng/L (mean 3.4 ng/L), ND (not detected)-1.2 ng/L (mean 0.5 ng/L) and 1.1-6.1 ng/L (mean 3.1 ng/L) outside Harbor (stations 13, 14), respectively. The mean concentrations of TBT, DBT and MBT inside Harbor where many vessels always anchor and ocean currents are relatively weaker due to a breakwater, were 3.9 times, 11.0 times and 4.1 times as high as those outside Harbor, respectively.

Comparing the concentrations of BTs in this study area with those in other areas in Korea were lower than those from Okpo Bay [TBT: 19-85 ng/L (mean 47 ng/L); DBT: ND-59 ng/L (mean 25 ng/L); MBT: 12-66 ng/L (mean 40 ng/L)] (Hong, 1996), Masan Bay [TBT: ND-59 ng/L (mean 23 ng/L); DBT: ND-91 ng/L (mean 29 ng/L); MBT: ND-720 ng/L (mean 109 ng/L)] (Choi et al., 1997), and were higher than those from Kwang Bay [TBT: ND-15.7 ng/L (mean 2.5 ng/L); DBT: ND-11.7 ng/L (mean 1.8 ng/L); MBT: ND-11.0 ng/L (mean 1.9 ng/L)] (Kim, 1997). They were comparable to shellfish-culture areas in the Atlantic (TBT: <8-57 ng/L; DBT: 1-15 ng/L; MBT: <1-14 ng/L) (Tolosa et al., 1992).

Gibbs et al. (1988) showed that TBT has no effects on organisms at concentrations less than 0.5 ng Sn/L level. However, TBT concentrations in all the seawater samples from inside Jeju Harbor were found to exceed this level. In fact, all of them showed TBT concentrations over 2 ng Sn/L which the UK has set as the Environmental Quality Status for TBT in seawater. The highest concentration of TBT, 40.9 ng/L, was observed at station 4 in June.

Comparing the mean BT concentrations with survey time (March, June and August) inside harbor, they showed different distribution patterns: 17.4 ng/L, 17.0 ng/L, and 5.7 ng/L for TBT; 0.8 ng/L, 12.3 ng/L, and 3.3 ng/L for DBT; 2.9 ng/L, 7.2 ng/L, and 36.7 ng/L for MBT. The concentrations of TBT, DBT and MBT were the highest in March, June, and

August, respectively. Each mean concentration ratio of TBT, DBT, and MBT to total BTs was 82%, 4%, and 14% in March, 46%, 33%, and 21% in June and 16%, 7%, and 77% in August, i.e., the main species was TBT in March and June, MBT in August (Fig. 3). This result shows the degradation of TBT based on antifouling paints with survey time or inputs of DBT/MBT.

Looking into the mean concentrations of total BTs with station, they did not show a distinct trend. They were about 60 ng/L at station 5, in the range of 40-50 ng/L at stations 4 and 10, about 35 ng/L at stations 3 and 6, about 27 ng/L at stations 8 and 11, and about 20 ng/L at other stations.

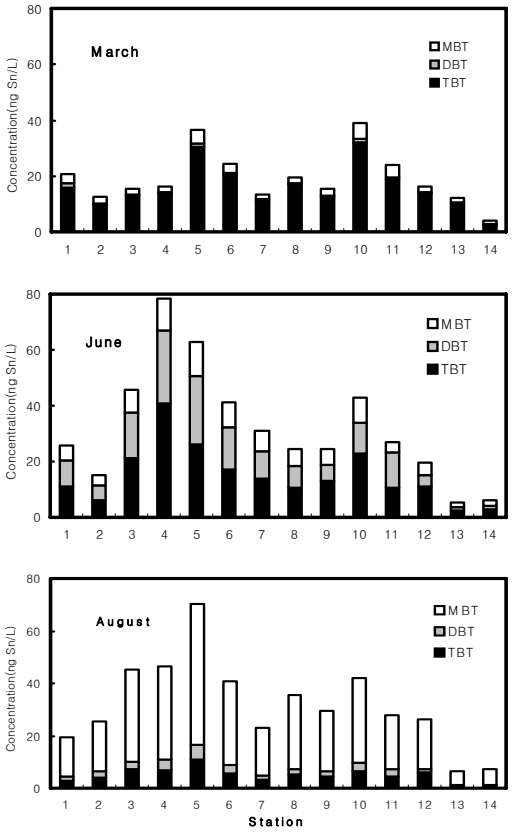

Fig. 2. Concentrations of BTs in seawater.

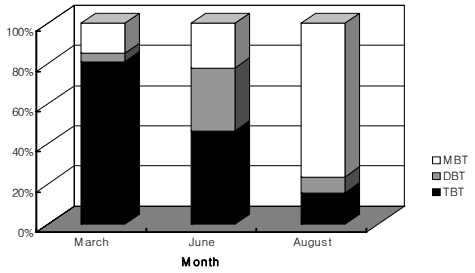

Fig. 3. Each mean concentration ratio of TBT, DBT, and MBT to total BTs in seawater.

The correlations between BTs were investigated in order to know that they were originated from other pollutants except for TBT based on antifouling paints (Table 1). The correlation coefficients between BTs were very high (0.73-0.83 for TBT/ DBT; 0.81-0.94 for TBT/MBT; 0.73-0.87 for DBT/MBT), indicating that DBT and MBT were mainly degraded from TBT and their sources were negligible.

Table 1. Correlation coefficients between BTs in seawater

	March			June			August		
	TBT	DBT	MBT	TBT	DBT	MBT	TBT	DBT	MBT
TBT		0.73	0.81		0.83	0.81		0.78	0.94
DBT	0.73		0.73	0.83		0.81	0.78		0.87
MBT	0.81	0.73		0.80	0.81		0.94	0.87	

BTs in 12 sediment samples inside Jeju Harbor were analyzed and the results are shown in Fig. 4. BTs were detected in all sediment samples and total BT concentrations at inner parts were higher than at outer parts, irrespective of survey time. The concentrations of TBT, DBT and MBT during all the survey times were in the range of 19-152 ng/g (mean 67 ng/g), 29-251 ng/g (mean 108 ng/g) and 6-57 ng/g (mean 24 ng/g), respectively. The concentrations of BTs in this study were generally lower than those from Okpo Bay [TBT: 5-2650 ng/g (mean 483 ng/g); DBT: ND-307 ng/g (mean 76 ng/g); MBT: ND-309 ng/g (mean 74 ng/g)] (Hong, 1996), Ulsan Bay (TBT:

26-13300 ng/g; DBT: ND-5090 ng/g; MBT: ND-1390 ng/g) (Shim et al., 1996), and were much higher than those from Kwangyang Bay [TBT: ND-8.5 ng/g (mean 3.5 ng/g); DBT: ND-1.5 ng/g (mean 0.1 ng/g); MBT: ND] (Kim, 1997). They were comparable to those from Chinhae Bay [TBT: 4-382 ng/g (mean 60 ng/g); DBT: 10-573 ng/g (mean 77 ng/g); MBT: 4-740 ng/g (mean 121 ng/g)](Shim, 1996), Masan Bay [TBT: ND-233 ng/g (mean 66 ng/g); DBT: ND-197 ng/g (mean 36 ng/g); MBT: ND-684 ng/g (mean 68 ng/g)] (Choi et al., 1997), Severn Sound in Ontaro, Canada (TBT: ND-182 ng/g; DBT: ND-175 ng/g; MBT: ND-96 ng/g) (Wong and Chau, 1992).

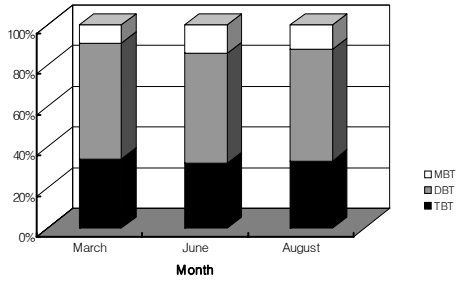

Fig. 4. Concentrations of BTs in sediments.

Comparing the BT concentrations with survey time (March, June, August), each BT concentrations showed similar distribution patterns irrespective of survey time, differently from those in seawater: 20-136 ng/g (mean 66 ng/g), 19-152 ng/g (mean 70 ng/g), and 27-146 ng/g (mean 65 ng/g) for TBT; 29-218 ng/g (mean 111 ng/g), 31-213 ng/g (mean 111 ng/g), and 38-251 ng/g (mean 103 ng/g) for DBT; 7-38 ng/g (mean 19 ng/g), 13-57 ng/g (mean 29 ng/g), and 12-51 ng/g (mean 23 ng/g) for MBT. Each mean concentration ratio of TBT, DBT and MBT to total BTs was 34%, 57%, and 10% in March, 33%, 52%, and 15% in June, and 34%, 54%, and 13% in August, i.e., the main species was DBT irrespective of survey time (Fig. 5), differently from that in seawater, which is considered that the degradation of TBT accumulated in sediment a long years ago [half life of TBT in sediment: 1.85 years (de Mora et al., 1989), >8-15 years (Astruc et al., 1990) or accumulation of DBT degraded from TBT due to its unstability in seawater [half life of TBT in seawater: 6-26 days (Seligman et al., 1988)]. This result is different from that from the south coast of Korea (the main species in sediment was TBT: TBT/DBT: 0,2-23.9) (Park and Hahn, 1996), Masan Bay (the main species in sediment was MBT in May, DBT in July and TBT in September) (Choi et al., 1997).

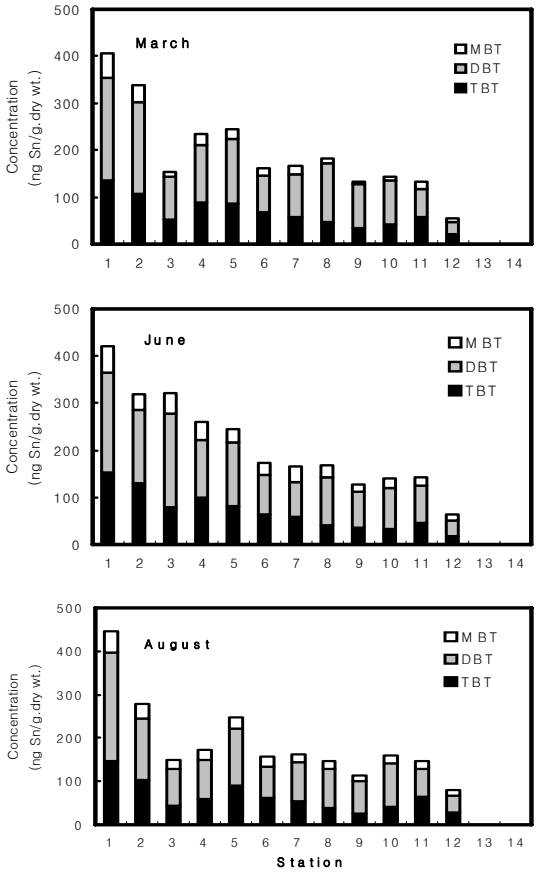

Fig. 5. Each mean concentration ratio of TBT, DBT, and MBT to total BTs in sediments.

Looking into the mean concentrations of BTs with station, total BTs were above 200 ng/g at stations 1-6, inner areas of a breakwater (station 7), where the mud-type sediment is mainly distributed. Especially the concentrations of TBT and DBT were above 100 ng/g and 140 ng/g, respectively at station 1 and 2.

The correlations between BTs were investigated (Table 2). The correlation coefficients were very high in the same way in seawater (0.70-0.81 for TBT/DBT; 0.77-0.93 for TBT/MBT; 0.75-0.83 for DBT/MBT), indicating that DBT and MBT were mainly degraded from TBT, and their sources were negligible.

Table 2. Correlation coefficients between BTs in sediments

	March			June			August		
	TBT	DBT	MBT	TBT	DBT	MBT	TBT	DBT	MBT
TBT		0.78	0.93		0.70	0.77		0.81	0.80
DBT	0.78		0.75	0.70		0.76	0.81		0.83
MBT	0.93	0.75		0.77	0.76		0.80	0.83	

The partition coefficient (K_d) was determined as concentration ratio between sediment and seawater (Tolosa et al., 1992) and calculated K_d values in this study are shown in Table 3.

A wide range of the K_d values are shown according to the difference in diverse organic matter, the size and binding affinity of particulates, etc (Batley, 1996). Generally it was known that the values were in the range of 227-55440 for TBT (Stang and Seligman, 1987), 2070-26080 for DBT and 1760-2870 for MBT (Stang and Seligman, 1987). The K_d values were in the range of 1283-52068 (mean 7944) for TBT, 4721-446659 (mean 73430) for DBT and 498-16257 (mean 4292) for MBT. In this study, the values of DBT and MBT were higher than those by Stang and Seligman (1987), which is considered to be due to the difference in sediment compositions and physical factors such as ocean currents and complex behaviors of BTs in seawater (Batley, 1996).

In order to evaluate the contribution of sedimentary organic matter to the BT concentrations in sediments, the correlation between sedimentary organic carbon content and TBT concentrations was also investigated (Fig. 6). No correlation coefficient (r=0.0028) was obtained between them in surface sediment. This result is similar to that from Chinhae Bay (Shim, 1996). Therefore, it was concluded that sedimentary organic matters could have little influence on the distribution of BTs in marine environment, in contrast with other hydrophobic contaminants (Farrington, 1991).

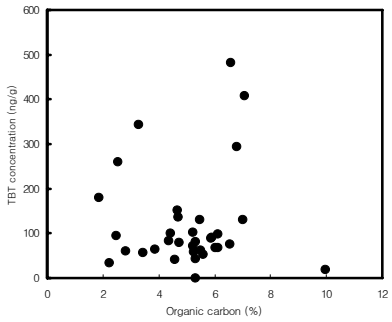

Fig. 6. Correlation between TBT concentration and organic carbon content in sediments.

Table 3. Partition coefficient (K_d, $BT_{sediment}/BT_{seawater}$) values of BTs

BTs	March	June	August	Total
TBT	1283-11073 (mean 4386)	1404-22062 (mean 5634)	4830-52068 (mean 13811)	1283-52068 (mean 7944)
DBT	66887-446659 (mean 151436)	4721-28376 (mean 11190)	22506-167000 (mean 45663)	4721-446659 (mean 73430)
MBT	1364-16257 (mean 7327)	2197-10660 (mean 4553)	498-3351 (mean 996)	498-16257 (mean 4292)

Fig. 7 shows the concentrations of BTs in three marine organisms, *T. clavigera*, *L. japonica* and *C. nigrolineata*. As they live in a limited area (A in Fig. 1) and their amounts are not sufficient, all collected samples for each organism were used for the analysis. The concentrations of TBT, DBT and MBT were in the range of 161-389ng/g [mean 268 ng/g (during all survey times), 334 ng/g (May, July, August)], 52-107 ng/g [mean 84 ng/g (during all survey times), 90 ng/g (May, July, August)], and ND-11 ng/g (mean 4 ng/g) for *T. clavigera*, 225-302 ng/g (mean 274 ng/g), 56-60 ng/g (mean 58 ng/g), and ND-13 ng/g (mean 4 ng/g) for *L. japonica*, 156-210 ng/g (mean 181 ng/g), 51-88 ng/g (mean 69 ng/g), and ND-16 ng/g (mean 9 ng/g) for *C. nigrolineata*. The BT concentrations for *T. clavigera* of this study were lower than those from Okopo Bay [TBT: 81-439 ng/g (mean 267 ng/g); DBT: ND-406 ng/g (mean 251 ng/g); MBT: 38-252 ng/g (mean 138 ng/g)] (Hong, 1996). TBT concentration was the highest in May for all the organisms among survey times and in *T. clavigera* among the organisms. For *T. clavigera*, TBT concentration during May to August, was about twice as high as those in March and April, which is considered that its spawning period is from May to September and it bioaccumulates BTs during this period, i.e., at its spawning period, the lipid content increases and BTs are hydrophobic compounds, thus the bioaccumulation of BTs in its lipid tissues increases. The metabolism of TBT in different organisms is known to be different for each species (Langston and Burt, 1991). Even for related groups occupying similar habitats, interspecific variations in TBT bioaccumulation potential are relatively large. Because only a few samples were analyzed, it is difficult to generalize the results.

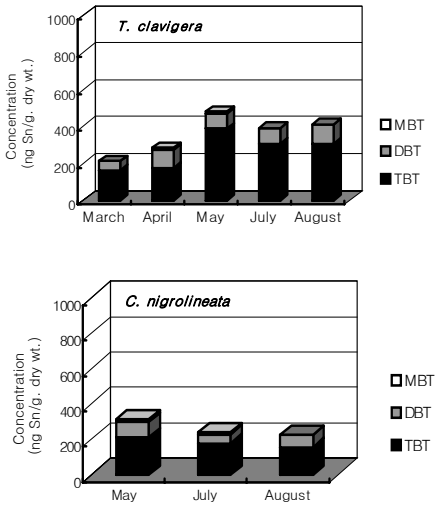

Fig. 7. Concentations of BTs in organisms.

Each mean concentration ratio of TBT, DBT, and MBT to total BTs were 78%, 21%, and 1% for *T. clavigera*, 81%, 18%, and 1% for *L. japonica*, and 70%, 27%, and 3% for *C. nigrolineata*, respectively, i.e., the main species was TBT (Fig. 8).

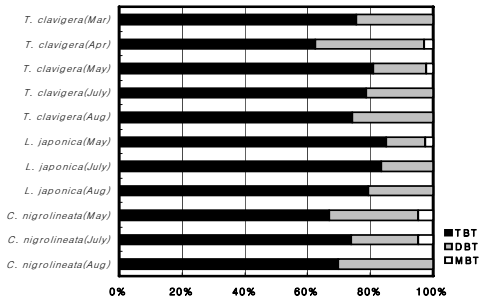

Fig. 8. Each mean concentration ratio of TBT, DBT, and MBT to total BTs in organisms.

The biological concentration factor (BCF) defined as $(BT)_{organism}/ (BT)_{sw}$, was determined from field study (Table 4). As BT concentrations show a great difference with survey time and the organisms used in this study live in a limited area, BCF was calculated in August when the sampling time is consistent for seawater and organism, with the results of BT concentrations in organism and mean BT concentration among the stations 1-7 (where are

adjacent to sampling station of organism). BCF values of TBT and DBT were in the range of 27,070-52,590 and 14,750-26,100, respectively. On the other hand, no BCF values for MBT were obtainable, because MBT was not detected in the organisms at the sampling time. Among the organisms, BCF values were in the order of *T. clavigera*> *L. japonica*>*C. nigrolineata* for TBT and *T. clavigera*>*C. nigrolineata* >*L. japonica* for DBT, i.e., The BCF values for TBT and DBT were the highest in *T. clavigera*. Shim (1996) reported that TBT bioaccumulation was different according to organism, i.e., he observed TBT concentration in *Crassostrea gigas* reflected TBT levels in water, indicating that TBT in water was a primary source for oyster, but TBT concentrations in *T. clavigera* were considered to be partially due to TBT in water because this organism is a kind of raptorial feeder. The BCF values of this study were higher than those from Okpo Bay (TBT: 4,830, DBT: 14,200 for *T. clavigera*; TBT: 5,510, DBT: 11,000 for *L. japonica*) (Hong, 1996), Chinhae Bay (TBT: 1,800-10,000 for *T. clavigera*) (Shim, 1996), which is considered to be due to a complex physical factors such as the ocean currents and the behavior of BTs.

Table 4. Biological concentration factor (BCF, $BT_{organism}$/ $BT_{seawater}$) values of BTs in organisms

	T. clavigera	*L. japonica*	*C. nigrolineata*
TBT	52,590	38,790	27,070
DBT	26,100	14,750	17,000
MBT	-	-	-

Lipid content in organism was determined to evaluate the contribution of lipid to partitioning of BTs (Fig. 9). A significant correlation (r=o.733) was observed between lipid content and corresponding TBT concentrations. This result is similar to that r=0.780) from Okpo Bay (Hong, 1996), but is different from Chinhae Bay, where no correlation was observed between them in oyster (Shim, 1996). He reported that TBT accumulation in oyster is not a simple function of lipid content, thus more various parameters have to be considered to account for partitioning behavior of BTs.

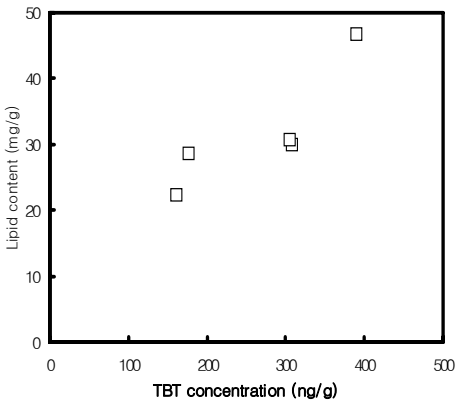

Fig. 9. Correlation between TBT concentrations and lipid content in *T. clavigera*.

Occurrence of imposex caused by BTs has been studied for many kinds of neogastropod species including *T. clavigera* (Gibbs and Bryan, 1986; Horiguchi et al., 1994). Imposex in *T. clavigera* was measured inside Jeju Harbor (Table 5). Rate of occurrence of imposex was 100%. RPLI and RPSI which represent the degree of imposex were higher with the range of 83.5-99.6% and 58.1-98.8%, respectively and were positively correlated with TBT concentrations. At the stage of imposex, the blockage of the pallial oviduct renders female sterile (Gibbs and Bryan, 1986). The darkened mass in capsule gland was observed in many female species, indicating females were sterile. Nevertheless, it is possible that this species do not exhibit a population decline because they have a planktonic stage as a veliger larva for about two months after hatching (Horiguchi et al., 1994). *T. clavigera* is a widespread species in Korea. Imposex on this species is sensitive

Table 5. Occurrence and degree of imposex in *T. clavigera*

	Sex ratio (m:f)	Mean shell Length (mm)	Mean penis length (mm)		Imposex Occurrence (%)	RPLI (%)*	RPSI (%)*
			male	female			
May	8:9	26.1	9.74	9.70	100	99.6	98.8
July	9:6	28.6	10.86	10.56	100	97.2	91.9
August	5:11	15.3	13.35	11.14	100	83.5	58.1

*RPLI(%): female penis length/male penis length ×100
*RPSI(%): female penis length^3/male penis length^3 ×100

to BTs. In addition, imposex can be measured in the field with no difficulty. Thus, the usage of imposex of *T. clavigera* in assessing the contamination of BTs may save money and time. Therefore, it could be recommended that imposex in *T. clavigera* may be used as a helpful tool of preliminary study for BTs in marine environment prior to trace elemental analysis.

4. Conclusions

The concentrations of BTs (TBT, DBT, and MBT) in seawater, sediments and organisms inside Jeju Harbor in 1998, were determined to assess the extent of contamination and to get some insight into the environmental fate and bioaccumulation of these contaminants. The occurrence and degree of imposex in *T. clavigera* were also measured to assess the sublethal effect of BTs on a marine gastropod.

The results obtained in this study indicated substantial contamination throughout inside Jeju Harbor where BTs levels were comparable to those from other coastal areas. In the correlations between the concentrations of TBT/DBT, TBT/MBT and DBT/MBT in seawater and sediments, the correlation coefficients were above 0.7, indicating that DBT and MBT were degraded from TBT based on antifouling paints and their sources were negligible.

No correlation coefficient between sedimentary organic carbon content and TBT concentrations in surface sediments was obtained, indicating that sedimentary organic matters could have little influence on the distribution of BTs in marine environment, in contrast with other hydrophobic contaminants.

The biological concentration factor (BCF, $BT_{organism}/BT_{seawater}$) values of TBT and DBT were in the range of 20,070-52,090, 14,750-26,100, respectively and were the highest in *T. clavigera* among the organisms.

A significant correlation (r=0.733) between TBT concentrations and lipid content in *T. clavigera* was observed in this study. This result was similar to that (r=0.780) from Okpo Bay, but different from that in oyster from Chinhae Bay, where no correlation was observed between them.

The rate of occurrence of imposex in *T. clavigera* was 100%. The RPLI and RPSI which represent the degree of imposex were high with the range of 83.5-99.6%, 58.1-98.8%, respectively and were positively correlated with TBT concentrations. Therefore, *T. clavigera* might be used as a biological indicator of BTs contamination. Measurement of imposex in *T. clavigera* is to be a very quick, cheap and helpful tool for a preliminary survey of BTs contamination studies.

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