Journal of the Korean Society of Oceanography
Vol. 33, No. 3, pp. 90—99, September 1998

Tributyltin and Triphenyltin Residues in Pacific Oyster (*Crassostrea gigas*) and Rock Shell (*Thais clavigera*) from the Chinhae Bay System, Korea

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Butyltin and phenyltin residues were quantified in seawater and biota of the Chinhae Bay System, Korea in 1995. Butyltin compounds were detected in all seawater and biota samples, whereas phenyltin compounds were found only in the biota samples. Tributyltin (TBT) concentrations in seawater ranged from < 8—35 ng Sn/l. Tributyltin concentrations in *Crassostrea gigas* and *Thais clavigera* ranged from 95—885 and 23—414 ng Sn/g, respectively. Triphenyltin (TPhT) concentrations in each species ranged 155—678 and 46—785 ng Sn/g, respectively. Spatial distribution of TBT was closely related to boating and dry-docking activities. However, spatial distribution of TPhT was not consistent with that of TBT. The biological concentration factor for TBT in *C. gigas* was about 25000 that is four times greater than that of *T. clavigera*. Butyl- to phenyltin concentration ratio was greater than one in *C. gigas*, but that in *T. clavigera* was less than one. Major tissues of *C. gigas* also showed different accumulation patterns for butyl- and phenyltin compounds. Furthermore, 19 and 28% of total body burdens of TBT and TPhT were found in gonadal mass of *C. gigas* just prior to spawning.

INTRODUCTION

Organotin compounds are among the most widely used organometallic chemicals. Since an organotin compound was first applied as a mothproofing agent in 1925 (Thompson *et al.*, 1985), an increasing number of organotin compounds have been produced for very diverse purposes. The two most important applications are heat stabilizers for synthetic polymers (*e.g.* PVC) and agricultural biocides. They also have been used as biocidal additives in antifouling paints to prevent adherence of sedentary organisms to ship hull and other structural surfaces immersed in water.

Organotins, in particular tributyltin (TBT) and triphenyltin (TPhT), have been recognized as dangerous chemicals giving deleterious effects on non-target marine organisms, since their adverse effects on oyster farming near marinas were revealed (Alzieu, 1986). A series of studies have demonstrated that organotin compounds are highly toxic to marine molluscs (Salazar and Salazar, 1991); they cause oyster shell anomalies and spat fall failure (Alzieu, 1986, 1991), reduced growth and viability of various larvae (Beaumont and Budd, 1984; Roberts, 1987), and imposex (imposition of male sexual organs on female) in neogastropods (Bryan *et al.*, 1986), even below ppb levels in seawater.

The major pathway of introduction of TBT and TPhT to the marine environment is through the use of these compounds as antifouling agents. These compounds are readily adsorbed onto solid surfaces (Dowson *et al.*, 1993). Organotin compounds have been shown to bio-concentrate in several marine organisms.

Since the early 1980s, most of industrialized countries have regulated the use of TBT as an antifouling agent for ships less than 25 m in length. However, there are no regulations in most of the Asian countries including Korea. In addition, organotin contamination near the Korean peninsula is not yet well investigated.

In the present study, the concentrations of TBT, TPhT, and their degradation products in seawater and biota of the Chinhae Bay System were determined to investigate the extent of contamination. Bioaccumulations of these compounds in two molluscs, *Crassostrea gigas* and *Thais clavigera*, were also evaluated to understand their partitioning behavior under a natural condition.

MATERIALS AND METHODS

Study area

The Chinhae Bay System is located on the south coast of Korea (Fig. 1). The system includes seven major areas: Masan Bay (M), Haengam Bay (H), Kadok Waterway (KW), Chindong Bay (C), Wonmunpo Bay (W), Kohyonsong Bay (K), and Chilchon Waterway (CW). A commercial harbor and a naval base are located in Masan Bay. There is a large shipyard in Kohyonsong Bay. Many small wharves for fishing boats are scattered along the coast of the Chinhae Bay System. Wonmunpo Bay and Chindong Bay have large oyster culture farms.

Sample collection

Biota and seawater samples were collected at 20 sites along the coast of the Chinhae Bay System in January 1995 (Fig. 1). *C. gigas* were also sampled at 2 sites (W4 and W5) in May 1995, just prior to spawning. *T. clavigera* were collected at 17 sites because they were not found at 3 sites (M1, M4, and C4). We selected the two species because they have different feeding behaviors (*C. gigas* for filter-feeder and *T. clavigera* for carnivore) and are widespread in the Korean seas. Seawater samples were taken from 16 of 20 sites at about 0.3 m below the surface to avoid the surface microlayer with acid-washed 1 l polycarbonate bottles which absorbed only meager amounts of tributyltin (Carter *et al.*, 1989). All the samples were frozen immediately on dry ice and transferred to the laboratory.

Analytical procedure

The analytical procedure of Stallard *et al.* (1989) is modified for this study; detailed procedure is available elsewhere (Shim *et al.*, 1998). The soft tissues removed from *C. gigas* and *T. clavigera* shells were respectively homogenized with a Tek-

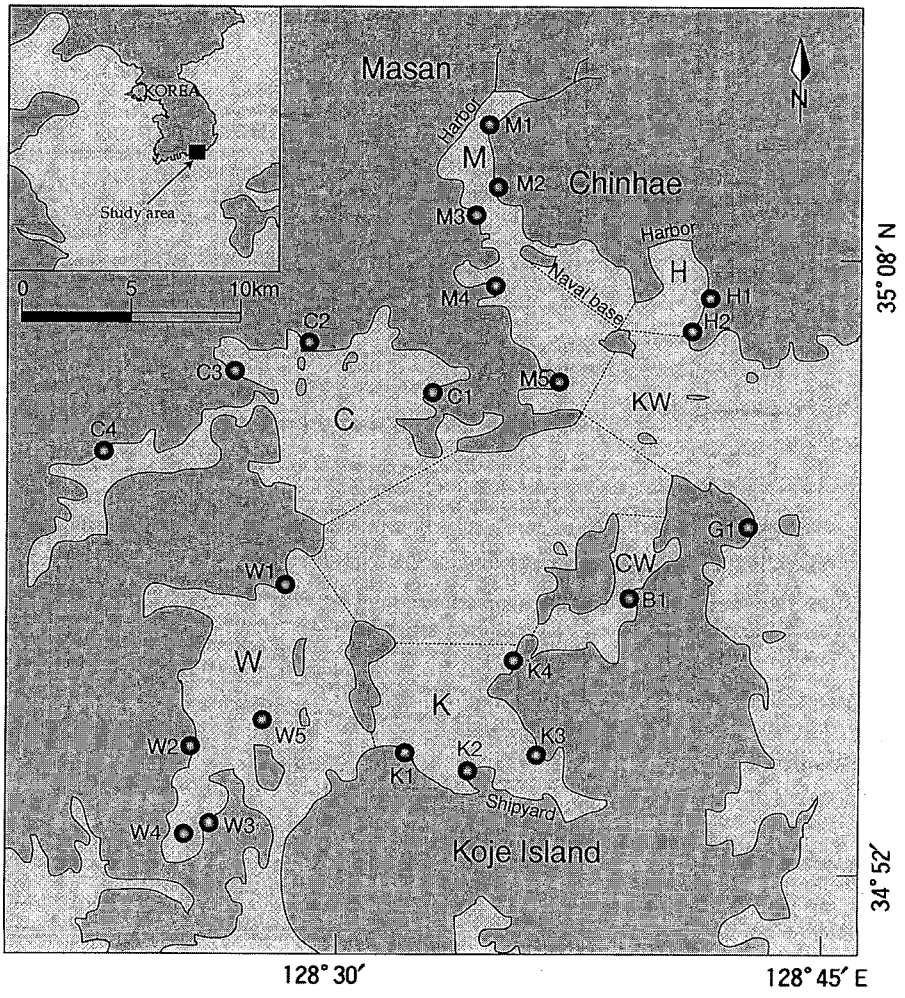

Fig. 1. Map of study area and sampling sites. M=Masan Bay, H=Haengam Bay, KW=Kadok Waterway, C=Chindong Bay, W=Wonmunpo Bay, K=Kohyonsong Bay, CW=Chilchon Waterway.

mar tissumizer. Tripentyltin chloride was added to samples as a surrogate standard. The samples were digested with 10 ml of 50% (v/v) HCl and then were extracted by shaking for 3 h with 20 ml dichloromethane. After 10 min centrifugation (4000 rpm), 2 ml of organic extracts were transferred to 15 ml glass test tubes and were concentrated under a gentle stream of nitrogen.

The concentrated extracts were re-suspended in 2 ml *n*-hexane and derivatized with 250 μl of 2M hexylmagnesium bromide for 20 min. The remaining hexylmagnesium bromide was neutralized with 4 ml of 0.4*N* sulfuric acid. The derivatized extracts were recovered by centrifugation and were cleaned up on 1 g of activated florisil. The cleaned extracts were concentrated again and spiked with tetrabutyltin as an internal standard, and then analyzed by gas chromatography using a flame photometric detector. The operating conditions of gas chromatograph are described in Shim *et al.* (1998).

After the tissue extraction, a 10 ml aliquot of organic extract was removed to a pre-weighed aluminum weighing pan. After standing for 48 h at room temperature, the pan weight was recorded to measure dichloromethane extractable lipid contents.

The frozen seawater samples were thawed. Hydrochloric acid was added to 800 ml of sample in a 1 l glass separatory funnel with a Teflon stopcock to adjust the pH to less than 2. In addition, the samples were spiked with tripentyltin chloride. To the funnel, 40 ml of dichloromethane was added. The funnel was shaken by hand for 2 min, vented, and then shaken on a reciprocating shaker for 10 min. The lower organic layer was removed into a flask. An additional extraction was conducted with 20 ml of dichloromethane. The organic layer was combined in the flask. Water in the organic extracts was removed by using anhydrous sodium sulfate and was concentrated under a gentle stream of nitrogen. The following procedure was same as the procedure for tissues.

Fresh standard stock solutions were made every three months. The whole analytical procedure was validated by analyzing reference materials (NIES11: sea bass, *Leteolabrax japonicus*) from the National Institute for Environmental Studies of Japan. The results of analysis of the reference materials fell within the range of the certified value for TBT (1.3 ± 0.1 μg/g, as chloride) and the reference value for TPhT (6.8 ± 0.6 μg/g, as chloride). Recoveries of organotin compounds from spiked (0.3 μg Sn/g) in *C. gigas* samples ranged from 71 to 98% for butyl- and phenyltin compounds. Reproducibility, as assessed by seven replicate extractions of oyster samples, was within less than 7% for butyltins and less than 15% for phenyltins. The detection limits of the whole analytical procedure for seawater ranged from 3 to 15 ng/l for butyl- and phenyltin compounds, and those for *C. gigas* ranged from 7 to 18 ng/g.

Concentrations of organotin compounds in this study are expressed as ng/g of Sn on a dry weight basis or ng/l of Sn to allow direct comparisons of the organotin compounds.

Statistics

A statistical function and curve fitting program (Excel 5.0 for PC, Microsoft) was used to obtain correlation coefficients between organotin concentrations and to draw curves of TBT concentrations in seawater and biota. Significances of correlation and linear regression analysis were obtained by analysis of variance from computer program (Mini-

Table 1. Butyltin concentraions (ng Sn/l) in seawater from the Chinhae Bay System

Site	MBT	DBT	TBT	Σ BT[1]
Masan Bay				
M1	13	30	32	75
M2	55	17	13	85
M3	19	6	19	44
M4	< 8	35	22	57
M5	11	< 3	9	20
Haengam Bay				
H1	51	30	30	111
H2	12	42	25	79
Chindong Bay				
C1	na[2]	na	na	na
C2	15	6	< 6	21
C3	na	na	na	na
C4	na	na	na	na
Wonmunpo Bay				
W1	13	6	12	31
W2	< 8	< 3	6	6
W3	< 8	11	27	38
Kohyonsong Bay				
K1	9	33	18	60
K2	< 8	8	28	36
K3	< 8	58	35	93
K4	na	na	na	na
Chilchon Waterway				
B1	8	13	< 6	21
Kadok Waterway				
G1	22	4	6	32

[1]Σ BT=TBT+DBT+MBT
[2]Not analyzed.

tab 7.0 for PC, Minitab Inc.).

RESULTS

Organotins in surface seawater

All the seawater samples contained detectable butyltins (Table 1). Phenyltins, however, were below detection limits at all sites. The overall ranges of butyltins in seawater were < 6 to 35, < 3 to 58, and < 8 to 51 ng/l for TBT, dibutyltin (DBT), and monobutyltin (MBT), respectively. The average values of TBT, DBT, and MBT concentrations in the study area were 18, 19, and 14 ng/l, respectively. The mean TBT composition was 39% of total butyltin in seawater in this study. Relatively high butyltin concentrations were found in Masan Bay, Haengam Bay, and Kohyonsong Bay.

Organotins in biota

The concentrations of butyl- and phenyltins in *C. gigas* collected in January 1995 are shown in Table 2. All the *C. gigas* samples analyzed from the Chinhae Bay System contained detectable butyl- and phenyltins. The overall ranges of TBT and TPhT concentrations in *C. gigas* were 95 to 885 ng/g (mean $\pm$ sd; 385 $\pm$ 217 ng/g) and 155 to 678 ng/g (323 $\pm$ 127 ng/g), respectively. The highest TBT concentration was observed at Site K3 in front of a large shipyard. TBT concentrations in *C. gigas* were relatively high at the innermost parts of Masan Bay, Kohyonsong Bay, Haengam Bay, and Wonmunpo Bay. DBT and MBT in *C. gigas* showed similar distribution patterns to that of TBT. TBT and DBT concentrations were highly correlated ($r^2=0.74$; $p<0.001$) as were DBT and MBT ($r^2=0.77$; $p<0.001$). These correlations among butyltins demonstrate that DBT and MBT are degradation products of TBT.

Phenyltins in *C. gigas*, however, showed different distribution pattern from that of TBT. No significant correlations ($p<0.05$) were obtained among TPhT, diphenyltin (DPhT), and monophenyl-

Table 2. Organotin concentrations (ng Sn/g dry wt.) in *C. gigas* from the Chinhae Bay System

Site	MBT	DBT	TBT	MPhT	DPhT	TPhT	Σ BT[1]	Σ PhT[2]	Σ OT[3]
Masan Bay									
M1	64	120	645	< 15	40	284	829	324	1152
M2	34	69	431	< 15	69	317	534	386	920
M3	35	71	498	< 15	30	155	604	185	789
M4	41	82	474	126	145	349	597	620	1218
M5	29	33	204	< 15	25	307	266	333	599
Haengam Bay									
H1	32	105	585	< 15	22	395	722	417	1139
H2	26	67	414	< 15	< 18	250	507	250	757
Chindong Bay									
C1	30	35	222	< 15	< 18	316	287	316	603
C2	26	22	95	52	23	407	142	482	625
C3	27	32	185	< 15	18	227	243	245	488
C4	39	29	138	< 15	31	319	206	350	555
Wonmunpo Bay									
W1	40	54	182	< 15	31	586	277	617	894
W2	63	67	261	99	40	378	391	517	908
W3	40	105	545	< 15	81	678	690	759	1450
Kohoynsong Bay									
K1	63	99	596	82	36	329	758	447	1205
K2	55	98	644	< 15	30	216	797	245	1042
K3	123	281	885	< 15	33	188	1289	221	1510
K4	18	49	264	< 15	30	317	331	347	678
Chilchon Waterway									
B1	18	39	195	< 15	< 18	212	252	212	464
Kadok Waterway									
G1	61	82	235	< 15	< 18	227	378	227	605

[1]Σ BT=TBT+DBT+MBT
[2]Σ PhT=TPhT+DPhT+MPhT
[3]Σ OT=Σ BT+Σ PhT

Table 3. Organotin concentrations (ng Sn/g dry wt.) in *T. clavigera* from the Chinhae Bay System

Site	MBT	DBT	TBT	MPhT	DPhT	TPhT	Σ BT[1]	Σ PhT[2]	Σ OT[3]
Masan Bay									
M1	ns[1]	ns	ns	ns	ns	ns	ns	ns	ns
M2	20	87	86	< 15	113	491	193	604	797
M3	27	89	131	< 15	154	387	247	541	788
M4	ns	ns	ns	ns	ns	ns	ns	ns	ns
M5	19	53	62	< 15	60	266	134	326	460
Haengam Bay									
H1	16	99	142	< 15	115	395	257	509	767
H2	10	51	59	< 15	< 45	238	120	283	402
Chindong Bay									
C1	21	44	45	< 15	39	142	110	181	291
C2	15	42	48	< 15	92	116	105	208	131
C3	24	76	129	< 15	38	358	229	395	624
C4	ns	ns	ns	ns	ns	ns	ns	ns	ns
Wonmunpo Bay									
W1	37	66	56	< 15	361	785	159	1147	1305
W2	23	73	55	< 15	99	380	151	480	631
W3	35	139	182	< 15	177	502	355	679	1034
Kohoynsong Bay									
K1	20	174	178	< 15	58	358	372	416	788
K2	26	129	269	< 15	59	259	425	318	743
K3	78	321	414	< 15	60	244	814	304	1117
K4	18	76	95	< 15	37	170	189	207	396
Chilchon Waterway									
B1	23	76	186	< 15	82	281	284	364	648
Kadok Waterway									
G1	10	16	23	< 15	16	46	50	62	112

[1]No samples were collected.

tin (MPhT) in *C. gigas*. The highest TPhT concentration was found at Site W1. TPhT levels were relatively high in Wonmunpo Bay and Masan Bay (Table 2). In comparison with TBT in *C. gigas*, TPhT levels were high in Chindong Bay and Wonmunpo Bay, but low in Masan Bay and Kohyonsong Bay. TPhT concentrations in *C. gigas* exceeded TBT concentrations at all the sites in Wonmunpo Bay and Chindong Bay including three other sites (M5, K4, and B1). DPhT concentrations were less than 100 ng/g except Site M3, and no detectable DPhT was found at Sites B1 and G1. MPhT was detected at just four sites (M3, C2, W1, and W2).

At all the sites, butyl- and phenyltins except MPhT were detected from *T. clavigera*. The ranges of TBT and TPhT levels in *T. clavigera* were 23 to 414 ng/g (mean$\pm$sd; 127$\pm$99 ng/g) and 46 to 785 ng/g (319$\pm$174 ng/g), respectively (Table 3). Spatial distributions of TBT and TPhT in *T. clavigera* are similar to those of *C. gigas*. The maximum TBT level (414 ng/g) in *T. clavigera* was found at Site K3. The overall TBT concentrations were also high in Kohyonsong Bay. The highest concentration of TPhT in *T. clavigera* was found at Site W3 near small wharf for fishing boats. TPhT levels were relatively high in Wonmunpo Bay.

TBT concentrations in both *C. gigas* and *T. clavigera* were positively correlated ($r^2=0.66$; $p<0.001$). The average TBT concentration in *T. clavigera* was about one-fourth of *C. gigas*. In case of TPhT, the average concentration in each species was almost same, and the correlation coefficient ($r^2=0.37$; $p<0.01$) was relatively low.

The composition of organotin compounds was different in *C. gigas* and *T. clavigera* (Fig. 2). Both TBT and TPhT were major organotin compounds in *C. gigas*. TBT accounted for 76% of total butyltin concentrations in *C. gigas*, whereas TBT accounted for 52% of total butyltin concentrations in *T. clavigera*. TPhT compositions in both organisms were more than 75%. Meanwhile, total butyltin and total phenyltin compositions in both organisms showed a reverse pattern. The average TPhT/TBT concentration ratio in *T. clavigera* was almost double in comparison with that in *C. gigas*.

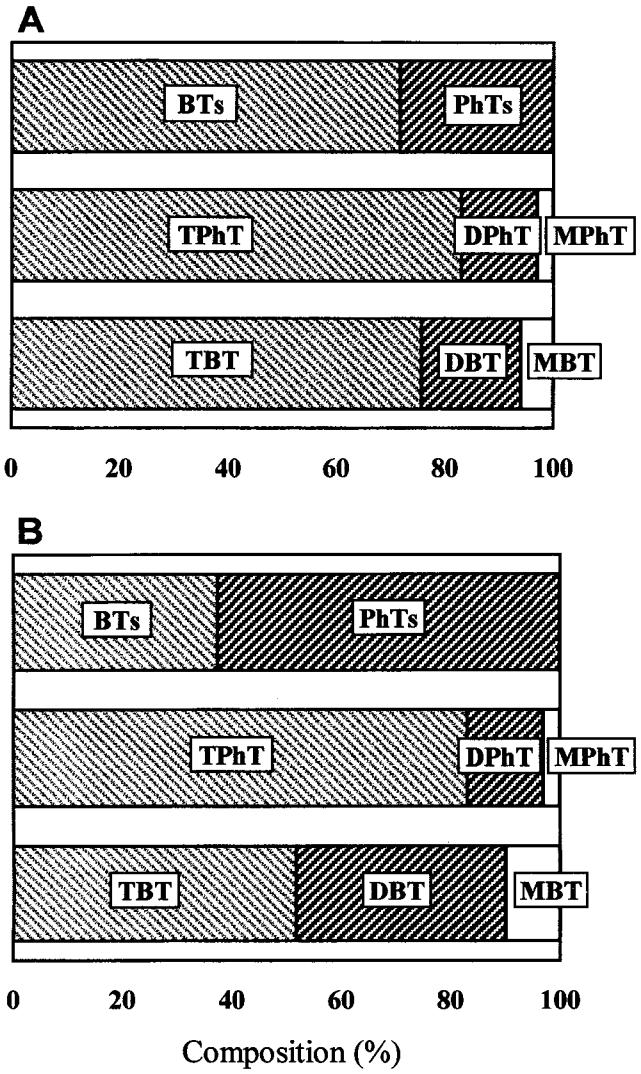

Fig. 2. Percent composition of butyl- and phenyltin concentrations in *C. gigas* (**A**) and *T. clavigera* (**B**).

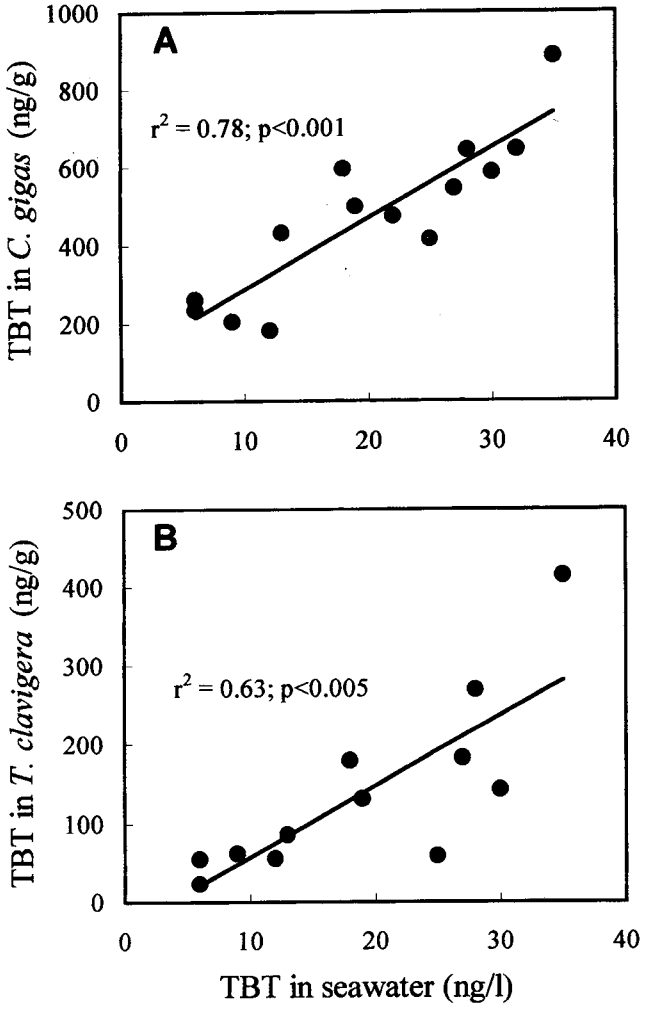

Fig. 3. Relationships between TBT concentrations in surface water and biota: (**A**) *C. gigas*, (**B**) *T. clavigera*.

TBT concentrations in seawater were more strongly correlated with TBT levels of *C. gigas* than those of *T. clavigera* (Fig. 3). TBT concentrations in *C. gigas* reflected the water TBT levels, indicating that TBT in water was a primary source for *C. gigas*. TBT concentrations in *T. clavigera* are thought to be partially due to TBT in water because this organism is a kind of raptorial feeder.

Bioaccumulation of organotins

The partition coefficients between seawater and biota were calculated from the field data. The biological concentration factors (BCF=[TBT in biota]/[TBT in water]) of butyltins in *C. gigas* and *T. clavigera* ranged *ca.* 16000 to 43000 and 1800 to 10000, respectively (Fig. 4). The average of BCF in *C. gigas* was *ca.* 25000 which was about four times greater than that of *T. clavigera* (BCF=6700). However, no BCFs for TPhT were obtainable, because TPhT was not detected in seawater at the time of sampling.

The distribution of organotins among the major tissues of *C. gigas* from four sites (K2, K3, W4, and W5) was determined to reveal to what extent each compound was accumulated in each compartment. High portions of TBT were found in the gill at Sites K2 and K3 and in the visceral mass at Sites W4 and W5 (Table 4), but TPhT concentrations reached a maximum in the visceral mass at all the sites. The lowest amounts of TBT were found in the adductor muscle, and TBT and TPhT concentrations in the mantle and the gonadal mass fell the middle of the range.

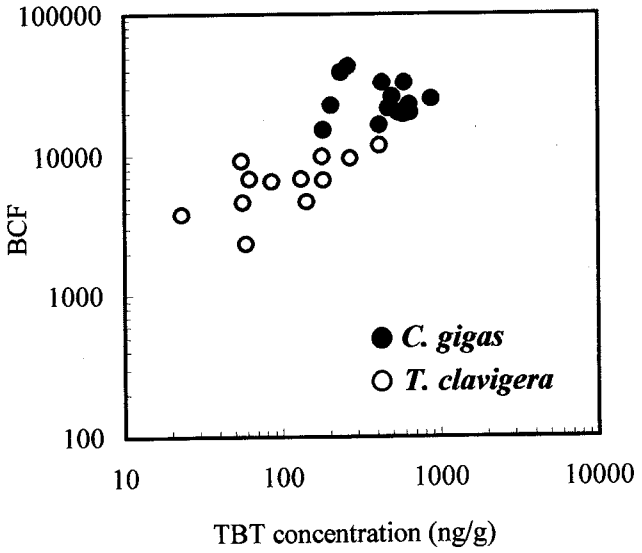

Fig. 4. Relationships between biological concentration factors (BCFs) and concentrations of TBT in *C. gigas* and *T. clavigera*.

Table 4. TBT and TPhT concentrations and dichloromethane extractable lipid contents in the major tissues of *C. gigas* from the four sites in the Chinhae Bay System

		Adductor muscle	Mantle	Gill	Gonadal mass	Visceral mass
Lipid (%)		1.5	13.2	9.1	11.2	15.7
TBT (ng/g)	K2	76	881	1020	na[1]	748
	K3	267	969	1510	na	1110
	W4	45	263	398	285	581
	W5	60	303	443	391	713
TPhT (ng/g)	K2	< 14	117	118	na	119
	K3	< 14	87	130	na	439
	W4	< 14	90	115	89	213
	W5	< 14	25	34	45	335

[1]Not analyzed.

Lipid contents (dichloromethane extractable) in major tissues of *C. gigas* were also determined to evaluate the contribution of lipid to the partitioning of organotins. No significant correlation ($p<0.05$) was observed between the tissue distribution of triorganotins and the corresponding concentrations (Table 4), so that it may be concluded that partitioning of organotins among major tissues in *C. gigas* was not the simple function of lipid content.

Separate collections of major *C. gigas* tissues were conducted just prior to spawning, and organotin concentrations in gonadal mass were determined at two sites (W4 and W5) to estimate the elimination of organotins (Table 4). Average TBT and TPhT burdens in gonadal mass observed at the two sites were 28 and 19% of total body burden, respectively. Therefore, 28% of total TBT body burden and 19% of total TPhT body burden were released from the body by the following reproductive process.

DISCUSSION

This study is the first report on contamination of TPhT as well as TBT in the Chinhae Bay System (Korea), a site of intense shellfish farming. TBT and TPhT concentrations in the system are comparable to those in other coastal areas of the world (Wade *et al.*, 1988; Higashiyama *et al.*, 1991; Tolosa *et al.*, 1992) when the concentrations were converted to tin basis. TBT concentrations in *C. gigas* were relatively high at the innermost sites of the sub-bays where harbors or shipyards were located. The primary source of TBT in the system is believed to be antifouling agent leached from ship hulls as is the case in other coastal areas (Dowson *et al.*, 1992; Tolosa *et al.*, 1992; Yonezawa *et al.*, 1993).

In contrast to TBT, occurrence and fate of TPhT in marine environment are not well known (Fent and Hunn, 1991). Thus far, only limited data on TPhT have been available. TPhT was detected in biota with concentrations up to 678 ng/g in this study. TPhT concentration exceeded TBT concentration in *C. gigas* at 10 of 20 sites surveyed. Spatial distribution of TPhT in biota was not consistent with that of TBT. TBT and TPhT concentrations in *C. gigas* showed no significant correlation ($p<0.1$) in this study, which is different from the results of Higashiyama *et al.* (1991). TPhT has been used much less for antifouling paints than TBT. TBT levels in biota samples reported in literature were usually higher than those of TPhT (Tolosa *et al.*, 1992; Fent and Hunn, 1995; Stäb *et al.*, 1995) just except some (Higashiyama *et al.*, 1991). The higher TPhT/TBT ratios found in environmental samples than actually used in antifouling paints may be explained by the differences of accumulation and elimination efficiencies between TBT and TPhT compounds. In fact, the octanol water partition coefficient (log K_{ow}) of TBT was 3.3, which is lower than the TPhT value of 4.1 as the chloride (Thompson *et al.*, 1985). The half-life of TBT in organisms is shorter than that of TPhT under field conditions (Horiguchi *et al.*, 1995; Stäb *et al.*, 1995). Therefore, the relatively high TPhT/TBT ratios in marine environments may be due to the higher lipophilicity and longer half-life of TPhT with

respect to TBT. This explanation, however, is not sufficient to explain the large difference in spatial distribution of both compounds in *C. gigas*. Further studies for other sources of organotins than antifouling paints may complement the explanation on the difference of spatial distribution.

Not all the organotins exhibit the same behavior in all compartments (Tolosa *et al.*, 1992). There were apparently different ratios of TBT to total butyltin concentrations in water and biota. The ratio decreased from biota to water. It was concluded that the highest ratios of TBT/total butyltin and TPhT/total phenyltin found in biota were apparently attributable to their higher affinity for biota. On the other hand, low TPhT concentrations in seawater ($<$ 10 ng/l) imply either a higher hydrophobicity of TPhT with respect to TBT, or its faster degradation due to instability in water. TPhT was degraded more rapidly than TBT under light condition (Caricchia *et al.*, 1994). However, the former explanation is more likely because relatively high TPhT concentrations were found in the biota samples.

As the high K_{ow} of TBT and TPhT imply possibility of accumulation of these compounds in biota, many studies indicated TBT accumulation in various organisms (Bryan and Gibbs, 1991; Fent and Hunn, 1991). However, the bioconcentration factors vary widely within two orders of magnitude (Thompson *et al.*, 1985; Zuolian and Jensen, 1989; Slooten and Tarradellas, 1994). There has been no attempt to compare the accumulations of TBT and TPhT in bivalves and gastropods.

TBT and TPhT compounds showed apparent biological accumulation in molluscs in this study. The average BCF of 25000 for TBT in *C. gigas* in the present study is at the lower end of the range reported by Bryan and Gibbs (1991) in which BCF is between 25000 and 550 000 in several aquatic organisms. Slooten and Tarradellas (1994) calculated the highest BCF of 900 000 in fresh water bivalve, *Dreissena polymorpha* under a field condition. In earlier work with *C. gigas*, Ebdon *et al.* (1989) reported a BCF of 10000 in the field, which corresponds to about 50000 on dry weight basis (assuming 80% water content) and is higher than the result of this study. Habitat difference may also affect BCFs. The *C. gigas* samples of this study were taken from an intertidal zone. Therefore, periodic exposure to air during low tide may have reduced the chance to accumulate TBT from water, compared to *C. gigas* which are submersed in water all day. The average BCF for TBT in *T. clavigera* (6700) is much lower than 100 000 reported by Bryan *et al.* (1987) in tidal tank experiment with dog-whelk, *Nucella lapillus*.

T. clavigera occupies higher trophic level than *C. gigas* because the former is a carnivore and the later is a filter-feeder. Therefore, the higher BCF for TBT in *C. gigas* than that in *T. clavigera* means that there may no biomagnification of TBT through trophic levels. TBT is not highly biomagnified because the organisms at higher trophic level can usually metabolize TBT compound (Thompson *et al.*, 1985). This is also supported by the fact that the percent composition of DBT and MBT were higher in *T. clavigera* than those in *C. gigas* in the study area (Fig. 2).

The average TPhT/TBT ratio was higher in *T. clavigera* than in *C. gigas*. It is not evident whether accumulation or elimination contributed more to the high TPhT/TBT ratio in *T. clavigera*. However, we can get some insight from the relative composition between butyl- and phenyltin compounds in each organism. The lower TBT/DBT ratio observed in *T. clavigera* may imply the higher degree of metabolism of TBT. Oyster, *C. virginica*, is slower to metabolize tributyltin oxide than other selected organisms (Lee, 1985). Whereas, the biological half-life of TPhT in *T. clavigera* is longer than that of TBT (Horiguchi *et al.*, 1995). In addition, difference of bioavailability between TBT and TPhT may also has influenced on the composition of each compound. *T. clavigera* and *Monodonta labio* (Mesogastropoda) showed exceptionally high concentrations of TPhT with respect to lipid contents (Hong, 1996) among the eight aquatic organisms.

The partitioning of organotins among major tissues of *C. gigas* is not a simple function of lipid content in contrast to other hydrophobic contaminants (Widdows *et al.*, 1983), so various parameters have to be considered to account for partitioning behavior of these compounds. The metabolic pathway and fates of these compounds in biota have not been well known. Therefore, further study on accumulation and depuration mechanisms as well as metabolic pathway is required to know what mechanism controls the TBT and TPhT distribution among *C. gigas* tissues.

TBT and TPhT burdens in gonadal mass of *C. gigas* were 28% and 19% of total body burden, respectively. Although gonadal mass burdens of both compounds were observed at the only two sites, it appears that 28% and 19% of TBT and TPhT

body burdens would be lowered during spawning. This means that organotin concentrations in *C. gigas* would differ before and after spawning. Therefore, spawning has to be considered when oyster samples are collected for monitoring studies. *C. gigas* sampled after spawning period would show an underestimate of organotin contamination.

CONCLUSIONS

The TBT and TPhT concentrations in seawater and biota of the Chinhae Bay System indicate that the system is highly polluted by these compounds. The most important TBT point sources are associated with boating and dry-docking activities. However, sources other than antifouling paints are conjectured to account the distribution of TPhT in the Chinhae Bay System. TBT and TPhT show different accumulation characteristics among major tissues of *C. gigas* as well as between the two molluscan species. Furthermore, high burdens of TBT and TPhT in gonadal mass of *C. gigas* just prior to spawning indicate that the following reproductive processes may reduce the corresponding amount of these compounds as a depuration mechanism.

ACKNOWLEDGMENT

The study was supported by the "SGRP/PTRP: Problem-oriented technology development project for agriculture, forestry and fisheries" (Ministry of Agriculture and Forestry, Korea) and by Korea Ocean Research and Development Institute (BSPE 97609-00-1077-4). We thank S.H. Hong for her assistance in organotin analysis. Thanks extends to two anonymous reviewers for their helpful comments.

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Manuscript received December 1, 1997
Revision accepted June 9, 1998