Chapter 7
Current Status of Contamination by Organotins and Imposex in Prosobranch Gastropods in Korea

Hyeon-Seo Cho and Toshihiro Horiguchi

Abstract Organotin compounds are considered to be dangerous chemicals because of their deleterious effects on non-target marine organisms. In 2003, the use of TBT-based antifouling paints was totally banned in Korea, and the International Maritime Organization (IMO) proposed to extend the ban to almost all ocean-going vessels. In this study, the concentrations of organotins in the coastal environment are analyzed to illustrate the differences of these analyzed items in the periods before and after the IMO and Korean regulations, focusing on organotins concentrations in molluscan soft tissues and the imposex phenomenon in the rock shell (*Thais clavigera*), a gastropod species sensitive to organotin compounds, collected from the Korean coasts from 1995 to 1997 and 2002, and from 2005 to 2009. TBT and TPhT were dominant organotins. Higher organotin concentrations were observed in areas with frequent shipping activities, including regions adjacent to harbors or shipyards, than in areas away from shipping activities. Concentrations of TBT, TPhT, and their metabolites in tissue, imposex frequency, and relative penis length index and sterility ratio of rock shell specimens collected from the southern coast after the regulations for TBT- and/or TPhT-based antifouling paints were in place showed lower values than those before the regulations. Because of the continued occurrence of imposex in the rock shell populations after the regulations were established, it is necessary to carry out further studies to monitor organotin concentrations in tissues and imposex frequency of rock shell specimens along with evaluations of the organotins residues in seawater and sediment in Korean coastal areas.

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Abbreviations

MBT	monobutyltin
DBT	dibutyltin
TBT	tributyltin
MPhT	monophenyltin
DPhT	diphenyltin
TPhT	triphenyltin
IMO	International Maritime Organization
RPLI	relative penis length index

7.1 Introduction

Organotin compounds have been used worldwide in antifouling paints to prevent adherence of sedentary organisms to ship hulls and other structural surfaces immersed in seawater. Organotins such as tributyltin (TBT) and triphenyltin (TPhT) are considered to be dangerous chemicals because of their deleterious effects on non-target marine organisms. Particularly, the imposex phenomenon, a superimposition of male genital tracts (penis and vas deferens) on female gastropods, has been reported to occur at low concentrations of certain organotins such as TBT and TPhT. As of 2004, approximately 150 species of gastropods had been reported to be affected by imposex worldwide (Horiguchi 2009).

In Korea, national restrictions on the use of TBT-based antifouling paints were introduced in 2000 for small boats, and these paints were totally banned in 2003. In addition, the International Maritime Organization (IMO) proposed to extend the ban to almost all ocean-going vessels from 2003. In the case of persistent substances in the environment, such as organotin compounds, their fate in the environment before and after the regulations were instituted is an important issue. In this study, the concentrations of organotins in the coastal environment are described and discussed to illustrate the differences of these analyzed items in the periods before and after the IMO and Korea regulations in 2003, focusing on their concentrations in molluscan soft tissues and imposex phenomenon of the rock shell (*Thais clavigera*), a gastropod species sensitive to organotin compounds, collected from the Korean coasts from 1995 to 1997 and 2002, and from 2005 to 2009.

7.1.1 *Materials and Methods*

7.1.1.1 Sample Collection

We collected the rock shell, *Thais clavigera* (Muricidae, Gastropoda), at 43 sites along the Korean coast between October 1995 and August 1997, and at 37 sites from March to August 2002 (Fig. 7.1). From 2005 to 2009, the nationwide survey was carried out in 45 sampling sites from coastal areas of the West Sea, South Sea, and East Sea (Fig. 7.2). The sampling sites were slightly different between each sampling year, but most of the selected sampling points were located in the coastal areas where contamination by organotin compounds derived from shipping activities was expected. Rock shell specimens were collected in the intertidal bedrock areas in the Korean coast. The rock shell *Thais clavigera* is one of the most sensitive species to TBT or TPhT (Horiguchi et al. 1995) and therefore was used as a bioindicator for biological effects by TBT or TPhT (Horiguchi et al. 1997). The appearance of imposex has been also reported in other gastropods to reflect the degree of contamination of organotin compounds (mainly, TBT) released from antifouling paints (Gibbs et al. 1991; Stewart et al. 1992; Stroben et al. 1992; Wilson et al. 1993; Curtis 1994; Evans et al. 1994; Horiguchi et al. 1994).

Additionally, surface seawater, sediment, and several shellfishes, including the blue mussel (*Mytilus edulis*), Pacific oyster (*Crassostrea gigas*), grand jackknife clam (*Solen grandis*), manila clam (*Ruditapes philippinarum*), dosinia (*Dosinia japonica*), venus clam (*Meretrix lusoria*), surf clam (*Mactra veneriformis*), ark clam (*Tegillarca granosa*), comb pen shell (*Atrina pectinate*), blood clam (*Scapharca broughtonii*), Chinese freshwater mussel (*Lanceolaria grayana*), trough clam (*Spisula sachalinensis*), and sandy beach clam (*Gomphina melanaegis*) were also collected at several sites on the coastal area of Korea from June to November 2000. We also investigated the seawater and sediment contamination levels by organotins in Busan and Ulsan harbors, using seawater and sediment samples collected at both harbors in 2002. Busan and Ulsan harbors are known as

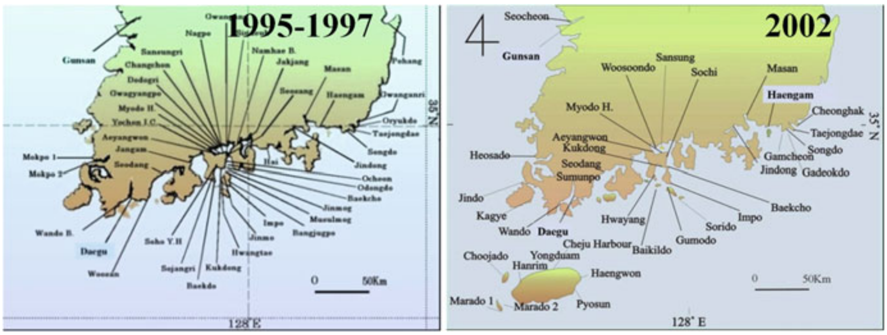

Fig. 7.1 Map showing the sampling sites of rock shells, *Thais clavigera*, collected from the Korean coast from 1995 to 1997 and in 2002

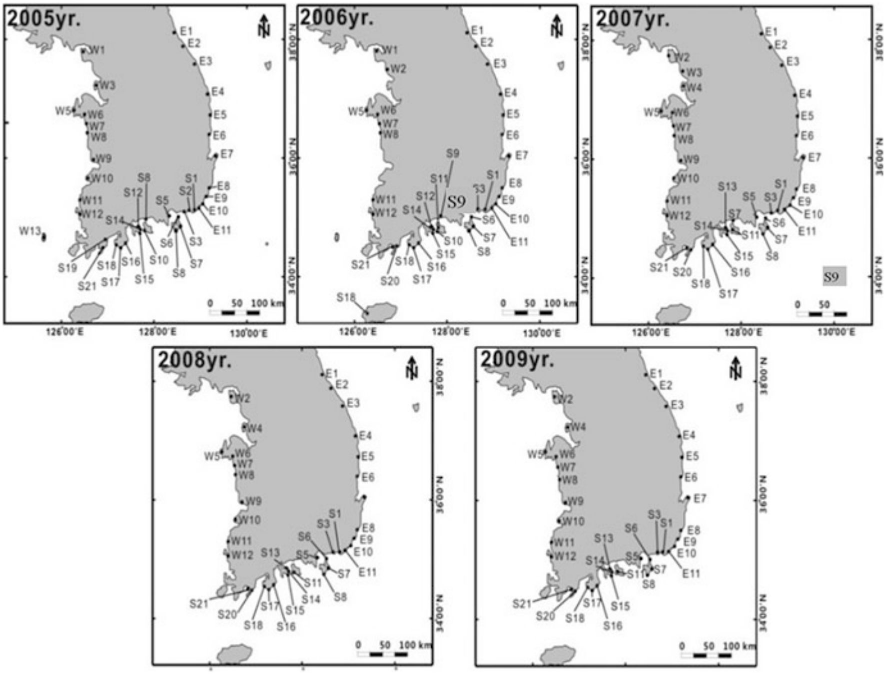

Fig. 7.2 Map showing the sampling sites of rock shells, *Thais clavigera*, collected from the Korean coast from 2005 to 2009 (Details on sampling location are shown in Table 7.1)

the biggest trade and industrialized harbors in Korea, respectively, which could have been the hotspot areas of organotins in Korea. Samples were kept at the freezer at −20 °C until chemical analysis for determination of organotin compounds.

7.1.2 Imposex Determination

According to the methods of Gibbs et al. (1987) and Horiguchi et al. (1994), sex was identified by the presence of female or male accessory sex organs: albumen gland, sperm-ingesting gland, and capsule gland for females, and prostate gland for males. Imposex was judged in female rock shells, based on the occurrence of a penis and development of vas deferens. Imposex was evaluated using the following indices: (1) percentage occurrence of imposex (imposex frequency = the number of imposex-exhibiting females/total number of females); (2) relative penis length index [RPLI (%)], which as calculated as the ratio (multiplied by 100) of the mean penis length in females to that in males at each location (Gibbs et al. 1987; Horiguchi et al. 1994); and (3) sterility, which as calculated as the ratio of total number of sterile females whose oviducts were blocked by vas deferens formation to total number of females (Horiguchi et al. 1994).

Table 7.1 Sampling sites of rock shell, *Thais clavigera*, collected from the Korean coast from 2005 to 2009

Eastern coast		Southern coast		Western coast	
E1	Sokcho, Gangwon-do	S1	Taejongdae, Busan metropolitan city	W1	Yeongjongdo, Incheon metropolitan city
E2	Jumunjin, Gangwon-do	S2	Gadeokdo, Busan metropolitan city	W2	Jamjindo, Incheon metropolitan city
E3	Samcheok, Gangwon-do	S3	Ungchon, Gyeongsangnam-do	W3	Jumundo, Incheon metropolitan city
E4	Jukbyeon, Gyeongsangbuk-do	S4	Deokdong, Gyeongsangnam-do	W4	Jebudo, Gyeonggi-do
E5	Hupo, Gyeongsangbuk-do	S5	Deokmyung, Gyeongsangnam-do	W5	Shinjindo, Chungcheongnam-do
E6	Yeongdeok, Gyeongsangbuk-do	S6	Guyeong, Gyeongsangnam-do	W6	Seosan, Chungcheongnam-do
E7	Guryongpo, Gyeongsangbuk-do	S7	Daegye, Gyeongsangnam-do	W7	Cheonbuk-myeon, Chungcheongnam-do
E8	Ulsan, Ulsan metropolitan city	S8	Haegeumgang, Gyeongsangnam-do	W8	Daecheon Harbor, Chungcheongnam-do
E9	Onsan, Ulsan metropolitan city	S9	Samchunpo, Gyeongsangnam-do	W9	Gunsan, Jeollabuk-do
E10	Ganjeolgot, Ulsan metropolitan city	S10	Seosang, Gyeongsangnam-do	W10	Gyeokpo, Jeollabuk-do
E11	Ilgwang, Busan metropolitan city	S11	Jicjang, Gyeongsangnam-do	W11	Gyema Harbor, Jeollanam-do
		S12	Industrial complex, Jeollanam-do	W12	Doripo, Jeollanam-do
		S13	Myodo, Jeollanam-do	W13	Heuksando, Jeollanam-do
		S14	Sindeok, Jeollanam-do		
		S15	Odongdo, Jeollanam-do		
		S16	Naro bridge, Jeollanam-do		
		S17	Dohwa, Jeollanam-do		
		S18	Poogyang, Jeollanam-do		
		S19	Usan, Jeollanam-do		
		S20	Maryang, Jeollanam-do		
		S21	Daegu, Jeollanam-do		

7.1.2.1 Determination of Organotin Compounds

After the imposex examination, tissue concentrations of six organotin compounds including monobutyltin (MBT), dibutyltin (DBT), tribultyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT), and triphenyltin (TPhT) were analyzed. The extraction procedure is as described in Horiguchi et al. (1994) and Choi et al. (2013), with some slight modifications. Briefly, organotins (butyltins and phenyltins) in homogenized biological samples were extracted with 0.1 % toropolone/benzene and 0.1 N HBr/ethanol. Then, extracts were derivatized with propylmagnesium bromide and cleaned up by silica gel column chromatography. Organotin compounds in these samples were measured by gas chromatograph-flame photometric detector (GC-FPD) (HP 5890A, Shimadzu GC-17A) or GC-mass selective detector (GC-MSD) (Shimadzu QP5050A, QP2010), and expressed as chloride, based on the internal standard method. Pretreatment procedures of organotin compounds in seawater and sediment were basically the same as mentioned but slightly modified (Ministry of the Environment, Japan). QA/QC was performed, using the certified reference materials of NIES CRM No. 11 and No. 12 (National Institute for Environmental Studies, Japan) for chemical analysis of butyltins and phenyltins in biological and sediment samples.

7.2 Results and Discussion

7.2.1 Organotin Pollution and Imposex in the Rock Shell in 1995 to 2002

From 1995 to 2002, imposex symptoms were evaluated in rock shell specimens from all sampling locations, but organotin concentrations in their soft tissues were determined only for some selected locations. From 1995 to 1997, organotin concentration (ng Sn/g wet wt.) ranges in rock shell specimens from 17 selected sampling locations were ND–90.6 (mean, 34.6) for TBT, ND–202.8 (mean, 87.2) for butyltins (BTs), ND–1086.0 (mean, 125.8) for TPhT, and ND–1163.9 (mean, 140.5) for phenyltin (PhTs). In 2002, organotin concentrations (ng Sn/g wet wt.) in rock shell specimens from 21 selected sampling locations ranged from 0.9 to 991.0 (mean, 121.5) for TBT, 1.0–2810.5 (mean, 381.5) for butyltins (BTs), ND–170.5 (mean, 26.7) for TPhT, and ND–276.2 (mean, 58.8) for PhTs. The mean compositions (%) of TBT among BTs were 38.2 % and 31.9 % for the period of 1995 to 1997 and 2002, respectively. The mean compositions (%) of TPhT among PhTs were 87.5 % and 51.3 % for the period of 1995–1997 and 2002, respectively.

In the first imposex survey conducted in Korea from 1995 to 1997, the frequency of imposex in rock shell populations was 100 % in almost all sites surveyed along the Korean coast. No imposex populations, that is, all females being normal in each population, were only observed in the population from Deukryang Bay located in the southwestern part of the South Sea, whereas the frequency of imposex was in the range 67–88 % close to the western part of the bay. The frequency of sterile individuals (with vaginal openings blocked by vas deferens formation) was higher (60 % or more) in the eastern part than in the western part of the South Sea. No sterile females were observed on the open-sea side and some other areas.

In 2002, the occurrence frequency of imposex in rock shell populations was 100 % in most of the sites surveyed along the South Sea coast. Although the frequency of occurrence of imposex in the rock shell populations from the Jeju coast was 0–100 %, no imposex populations were observed at two of eight sites surveyed in Jeju. Geographic distribution of the frequency of sterile individuals was similar to that of the first survey, and a higher frequency (60 % or more) of sterile individuals was found in the eastern part than the western part of the South Sea. No sterile females were found at 6 of 19 sites along the South Sea coast and at 5 of 8 sites surveyed in Jeju Island.

7.2.2 Concentrations of Organotins in Seawater, Sediment, and Other Shellfishes Collected in 2000 and 2002

In 2000, six organotin concentrations in shellfishes as well as seawater and sediment samples from the south and east coasts were relatively higher than those on the west coast. Average TBT concentrations in seawater and sediment samples were 8.1 ng Sn/l and 10.6 ng Sn/g wet wt., respectively. Average TBT concentrations in tissues of the shellfishes collected at the south and east coasts were 23.9 ng Sn/g wet wt. and 32.0 ng Sn/g wet wt., respectively. Species-specific accumulations of organotins in tissue were observed. The highest BTs (158.2 ng Sn/g wet wt.) and PhTs (20.1 ng Sn/g wet wt.) were found in the Pacific oyster. In addition, organotin concentrations in the Pacific oyster were generally higher than those in other shellfishes. MBT (mean, 2.8 ng Sn/g wet wt.), DBT (mean, 5.5 ng Sn/g wet wt.), TBT (mean, 50.5 ng Sn/g wet wt.), and TPhT (mean, 3.0 ng Sn/g wet wt.) were detected in all Pacific oyster specimens. The ranges of organotin concentrations (ng Sn/g wet wt.) detected in other shellfishes were as follows: ND–18.5 (mean, 2.7) for MBT, ND–21.4 (mean, 3.0) for DBT, ND–93.2 (mean, 17.3) for TBT, ND–0.6 (mean, 0.02) for MPhT, ND–0.2 (mean, 0.02) for DPhT, and ND–6.7 (mean, 1.1) for TPhT. Tributyltin (TBT) was a predominant butyltin species and accounted, on average, for 74.6 % of BTs in all analyzed shellfish specimens. Except for a comb pen shell and a trough clam sample, TPhT was predominant among PhTs and accounted, on average, for 89.4 % of PhTs in all analyzed shellfish specimens.

In the detailed survey for hotspot harbors conducted in 2002, TBT concentrations in the seawater of Busan and Ulsan harbors were in the range 1.3–12.7 (mean, 4.7) ng Sn/l and 4.8–46.6 (mean, 13.2) ng Sn/l, respectively. TBT concentrations in Nakdong River estuary were ND–1.6 (mean, 0.3) ng Sn/l. TPhT was also detected in seawater at several locations. The concentrations of TBT and TPhT in the sediment of Busan Harbor were 4.8–745.6 (mean, 187.2) ng Sn/g dry wt. and 0.4–10.7 (mean, 2.2) ng Sn/g dry wt., respectively. Much higher concentrations, of 203.1–556.7 μg Sn/g dry wt. of TBT and 2.2–3.9 μg Sn/g dry wt. of TPhT, were observed in sediment near a dockyard in Busan. The concentrations of TBT and

TPhT in sediment of Ulsan Harbor were 22.3–1042.9 (mean, 259.2) ng Sn/g dry wt. and 0.2–36.2 (mean = 5.6) ng Sn/g dry wt., respectively. TBT concentrations in sediment from the Nakdong River estuary were in the range 0.2–8.7 (mean, 1.6) ng Sn/g-dry wt. TBT concentrations in seawater and sediment samples varied regionally and also differed from those in shellfishes. High shipping activity, especially in the coastal/inshore areas, has brought about extensive contamination by organotin compounds, such as TBT and TPhT, suggesting the continuous contamination of organotin in the coastal waters of Korea in the sampling period.

7.2.3 Organotin Pollution and Imposex in the Rock Shell in 2005–2009

From 2005 to 2009, imposex symptoms and organotin concentrations in rock shell populations were analyzed using specimens sampled from all locations. In detail, the locations for sampling rock shell specimens were 39 in 2005, 37 in 2006, 2007, and 2009, and 36 in 2008. The range and mean concentrations of all six organotin compounds (ng Sn/g wet wt.) in rock shells collected from the West Coast were 6.6–36.1 (mean, 18.4) for 2005, 9.0–46.1 (mean, 24.1) for 2006, 2.3–57.4 (mean, 10.9) for 2007, 2.5–131.0 (mean, 24.8) for 2008, and 2.4–24.5 (mean, 13.6) for 2009. The range and mean concentrations of all six organotin compounds (ng Sn/g wet wt.) in rock shells collected from the South Coast were 12.8–138.0 (mean, 48.4) for 2005, 8.2–202.0 (mean, 49.7) for 2006, 4.8–45.7 (mean, 22.7) for 2007, 3.0–38.1 (mean, 21.7) for 2008, and 1.8–26.1 (mean, 6.4) for 2009. In the West Coast, the range and mean concentrations of all six organotin compounds (ng Sn/g wet wt.) in rock shells were 2.8–34.8 (mean, 13.9) for 2005, were 5.1–78.7 (mean, 20.0) for 2006, 4.8–35.8 (mean, 11.3) for 2007, 1.1–18.4 (mean, 6.0) for 2008, and 2.3–13.6 (mean, 6.5) for 2009.

The total of all six organotin concentrations in each sampling geographic area from 2005 to 2009 are shown in Fig. 7.3. On the east coast, the highest concentrations of organotins in rock shell specimens were found in Ulsan and Onsan. The concentrations of organotins in rock shell specimens collected from the south coast were found as two to three times higher than those in the west and east coast. On the south coast, the highest concentrations of organotins in rock shells were found in Busan and Yeosu. On the west coast, the highest concentrations of organotins in rock shells were found in Seosan, Daecheon Harbor, and Gyema Harbor, and relatively consistent organotin concentrations were found in other sampling locations.

In areas adjacent to a harbor or shipyard, concentrations of BTs consisted of ND–27.3 ng Sn/g wet wt. for MBT, ND–51.6 ng Sn/g wet wt. for DBT, and ND–34.2 ng Sn/g wet wt. for TBT. Concentrations of PhTs consisted of ND–4.4 ng Sn/g wet wt. for MPhT, ND–34.2 ng Sn/g wet wt. for DPhT, and ND–4.7 ng Sn/g wet wt. for TPhT. In addition, in other sampling areas, concentrations of BTs consisted

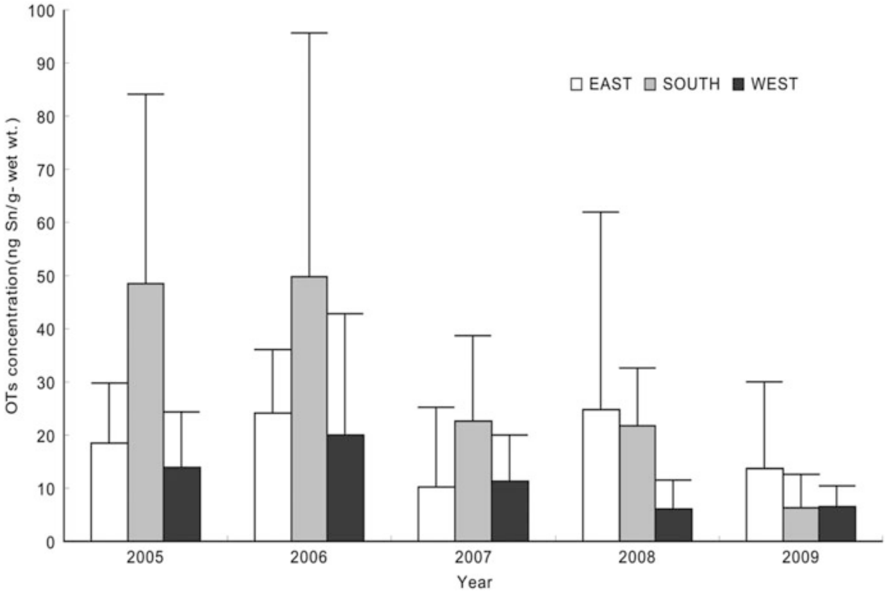

Fig. 7.3 Annual mean concentrations of all six organotin compounds in tissue of *Thais clavigera* from the Korean coast from 2005 to 2009

of ND–6.1 ng Sn/g wet wt. for MBT, ND–7.5 ng Sn/g wet wt. for DBT, and ND–8.0 ng Sn/g wet wt. for TBT, and concentrations of PhTs consisted of ND–1.4 ng ng Sn/g wet wt. for TPhT; MPhT and DPhT were not detected.

Higher concentrations of BTs than PhTs were found in both females and males of rock shell specimens. The total of all six organotin concentrations in females ranged from ND to 97.6 ng Sn/g wet wt. The concentrations of BTs in females showed the highest concentration in 2006 and a decreasing trend in 2007, 2008, and 2009. The average relative percent (%) composition in concentrations of MBT: DBT:TBT in total concentrations of BTs was 27.9:34.9:37.2, respectively. Of PhTs, only TPhT was detected in female individuals, and the concentration of TPhT increased from 2005 to 2007 and then decreased from 2007 to 2009.

Total of all six organotin concentrations in males ranged from ND to 105.0 ng Sn/g wet wt. BTs in males showed the highest concentration in 2006 and a gradually decreasing trend in 2007, 2008, and 2009. The average relative % composition in concentrations of MBT:DBT:TBT in total concentrations of BTs was 26.9:35.1:38.0, respectively. Regarding PhTs, the average relative % composition of MPhT:DPhT:TPhT was 12.7:0.1:87.2. In 2005, the highest composition ratio in total PhTs was found for MPhT, but was highest for TPhT in other sampling years.

7.3 Trends of Environmental Concentrations of Organotin Compounds and Imposex Phenomenon in Rock Shells Before and After the Korean Domestic and International Regulations for TBT- or TPhT-Based Antifouling Paints

The south coast is selected, because there are more data than from the east and west coasts, for comparing the concentrations of organotins before and after the Korean domestic and international regulations for TBT- and/or TPhT-based antifouling paints, based on local surveys from 1995 to 2009. It is worth noting that imposex symptoms were consistently observed in the rock shell populations collected at sampling locations along this south coast during the period (1995–2009), suggesting a sequence of organotin pollution related to vessel-related activities and its environmental impacts. Thus, the variation in environmental concentrations of organotins and imposex symptoms in the rock shell were investigated on the south coast on the basis of field surveys before (1995–1997 and 2002) and after (2005–2009) the Korean domestic and international regulations for TBT- or TPhT-based antifouling paints.

In the period 1995–2009, the range of six organotin concentrations detected in tissues of rock shell specimens collected from the south coast was 1.0–1651.0 ng Sn/g wet wt. The mean six organotins concentrations were found to be 193.0 ng Sn/g wet wt. for the periods of 1995–1996, 176.0 ng Sn/g wet wt. for 1997, 484.0 ng Sn/g wet wt. for 2002, 48.4 ng Sn/g wet wt. for 2005, 49.7 ng Sn/g wet wt. for 2006, 22.7 ng Sn/g wet wt. for 2007, 21.7 ng Sn/g wet wt. for 2008, and 6.4 ng Sn/g wet wt. for 2009. The highest organotin concentration was found for TPhT in 1995–1996 as 396.0 ng Sn/g wet wt. The concentrations of TPhT, however, rapidly decreased from 1995 to 2002 and from 2005 to 2009. On the other hand, the concentrations of TBT increased from 1995 to 2002 and then gradually decreased from 2005 to 2009.

All six organotin concentrations (ng Sn/g wet wt.) in tissues of each sex of rock shell specimens before the regulations were ND–873.0 (mean, 163.0) and 3.0–1791.0 (mean, 190.0) for females and males, respectively. Those concentrations after the regulations were 0.1–97.6 (mean, 15.5) and 0.1–105.0 (mean, 14.2) for females and males, respectively. Gender-specific difference in accumulation of organotins was unclear. Although there was a specific contamination by site, the mean organotin concentrations in tissues of female and male rock shell specimens from the south coast before the regulations were 11- and 13 fold higher than those after the regulations, respectively. The efficiency of the Korean domestic and international regulations for TBT- or TPhT-based antifouling paints seems clear. On the other hand, the proportions of detected concentrations of MBT, DBT, and TBT among BTs appeared to be consistent in both males and females before and after the regulations, and TBT accounted for a relatively higher proportion than other BTs. Additionally, TPhT was found to account for high proportions in total

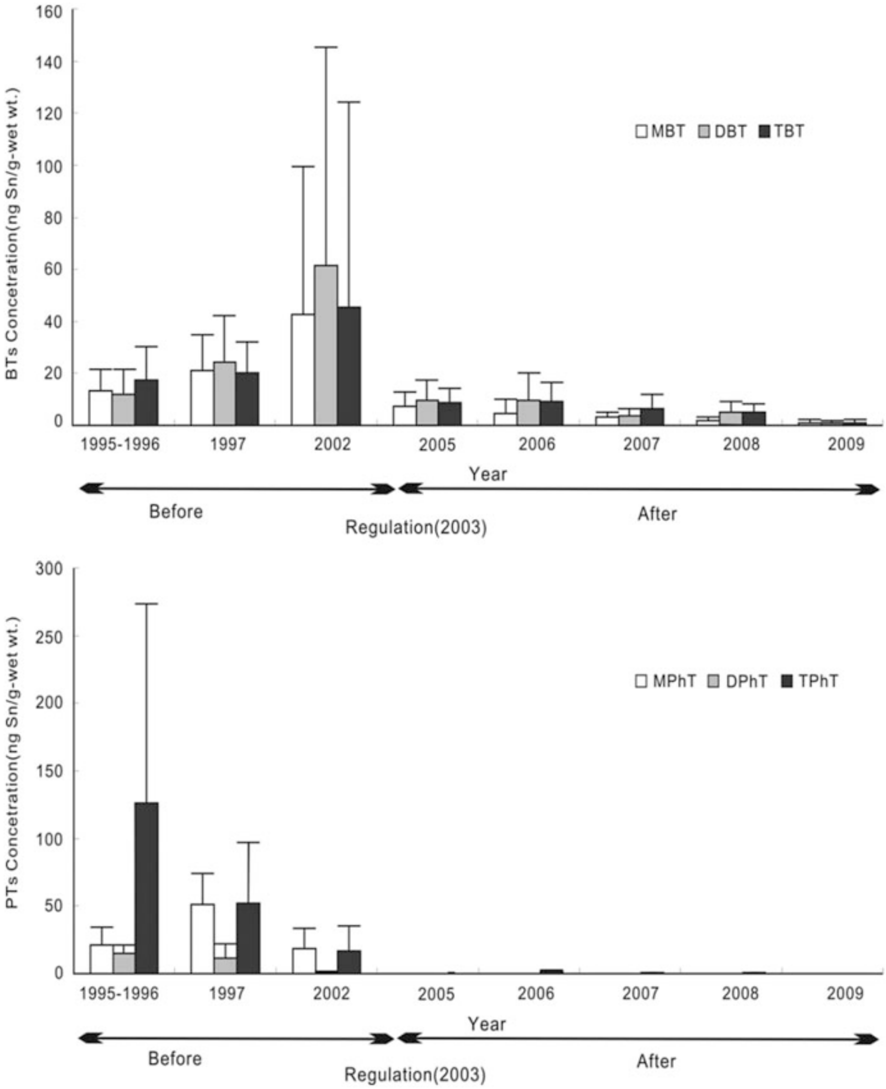

Fig. 7.4 Interannual variation of mean concentrations of butyltins (*upper*) and phenyltins (*lower*) in female *Thais clavigera* tissues from the southern coast, Korea

PhTs detected in both male and female rock shells, except for males in 2002 (Figs. 7.4 and 7.5).

Concentrations of six organotins in rock shell tissues collected from the south coast showed a gradually decreasing trend after the regulations and a relatively low residual concentration after 2007. However, the areas of Yeosu, Jinhae, and Busan had higher organotin concentrations than other areas, which may be attributed to the existence of local pollution sources. The interannual variation of imposex

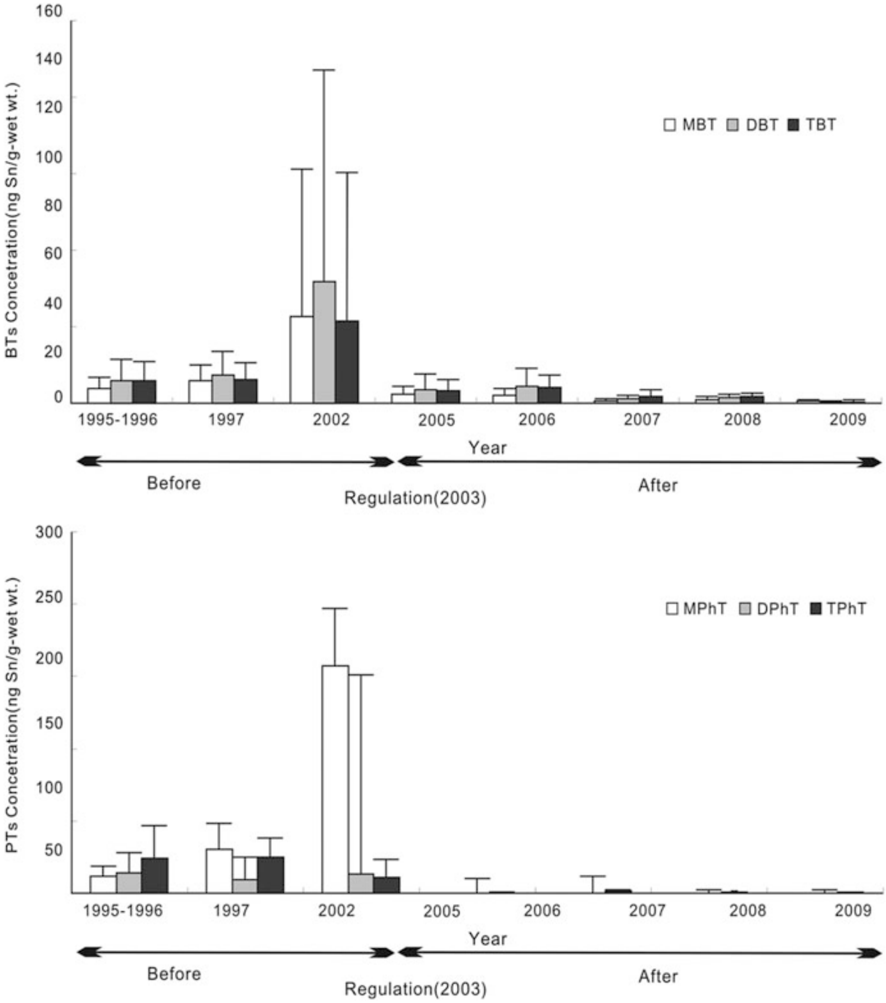

Fig. 7.5 Interannual variation of mean concentrations of butyltins (*upper*) and phenyltins (*lower*) in male *Thais clavigera* tissues from the southern coast, Korea

frequency, RPL index (RPLI), and sterility in the rock shells from the south coast is shown in Fig. 7.6. The imposex frequency in 1995–2009 ranged from 0 to 100 %. Before the regulations, except for some selected control areas in 1995–1996, the imposex frequency was 100 % until 2005 and gradually decreased from 2005 to 2009. This high imposex frequency in the rock shell from the south coast of Korea suggests it may be the result of the high sensitivity of the rock shell to TBT, whose imposex is induced by very low concentration of TBT (approximately 1 ng/l) in seawater (Horiguchi et al. 1995). The low or slow recovery rate from imposex in the rock shell from the south coast may imply a point source of contamination by

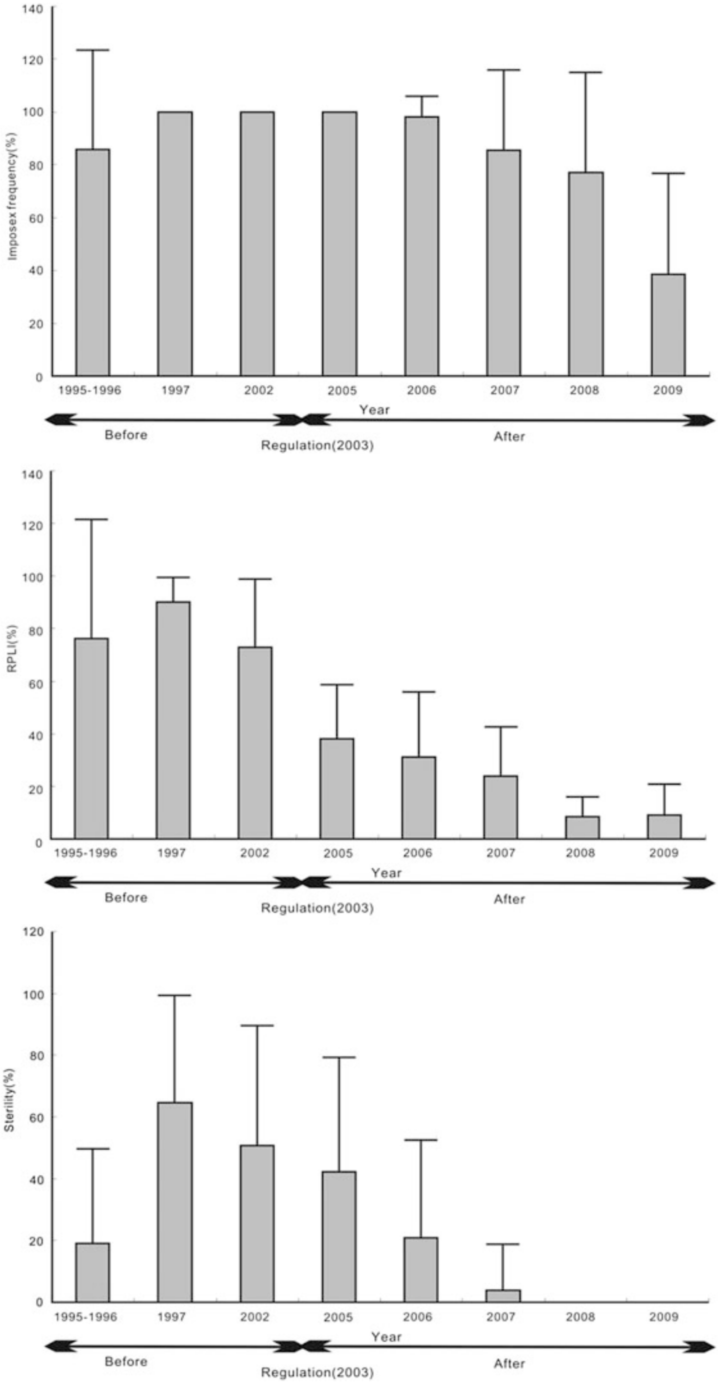

Fig. 7.6 Interannual variation of imposex frequency, RPL index (RPLI) and sterility in *Thais clavigera* from the southern coast, Korea

organotins resulting from the existence of many anchoring areas and shipping activities in this area.

The range of RPLI was 0–100 % in 1995 and 2009, and the mean of RPLI was 76.3 %, 93.0 %, 29.3 %, 38.1 %, 32.5 %, 23.6 %, 8.9 %, and 9.2 % in the period of 1995–1996, 1997, 2002, 2005, 2006, 2007, 2008, and 2009, respectively. RPLI before the regulations ranged from 0 to 149.0 % (mean, 62.4 %) and from 0 to 84.6 % (mean, 23.1 %) after the regulations. The mean RPLI after the regulations was found to be one third of that before the regulations.

The percentage occurrence of sterile females ranged from 0 to 100 % in the period from 1995 to 2009, and its mean value varied as 19.1 %, 64.7 %, 50.6 %, 42.4 %, 20.9 %, 3.8 %, 0 %, and 0 % in the period of 1995–1996, 1997, 2002, 2005, 2006, 2007, 2008, and 2009, respectively. The sterility ratio showed an increasing trend from 1995 to 2002, except for selected control sites in 1995, and showed a continuous decreasing trend after the regulations from 2005 to 2009.

7.4 Conclusions

TBT and TPhT were found to account for a high composition ratio in total butyltin and phenyltin concentrations, respectively. The higher concentrations of all six organotin concentrations were observed in areas with frequent shipping activities, including regions adjacent to harbors and shipyards than those in areas away from shipping activities.

In rock shell populations, the range of imposex frequency, RPLI, and sterility was 0–100 %, 0–84.6 %, and 0–100 %, respectively. Similar to the geographic distribution of all six organotin concentrations in seawater, the occurrence and degree of imposex were observed in rock shell specimens collected along the Korean coast (i.e., areas with frequent shipping activities such as harbors and shipyards, areas away from harbors, and ship-anchoring regions).

In summary, concentrations of TBT, TPhT and their metabolites in tissue, imposex frequency, and RPLI and sterility ratio of rock shell specimens collected from the Korean southern coast after imposition of the Korean domestic and international regulations for TBT- or TPhT-based antifouling paints showed lower values than those before the regulations. Thus, in general, efficiency of the Korean domestic and international regulations for TBT- and TPhT-based antifouling paints seems clear. However, it was also observed that these values were still high in areas adjacent to harbors or shipyards. Meanwhile, although concentrations of TBT and TPhT, which cause imposex in gastropods, continuously decreased after the regulations, increasing trends of concentrations of metabolites of TBT and TPhT (namely, MBT and DBT for TBT and MPhT and DPhT for TPhT) were found.

Because of the continued observation of the occurrence of imposex in rock shell populations, even after the regulations were established, it is necessary to carry out further field studies to monitor concentrations of organotins in tissues and imposex frequency in rock shell specimens in parallel with evaluations of the organotin residues in seawater and sediment in the coastal waters of Korea. It is also necessary to put more efforts into understanding the possible ecological impacts by other antifouling substances (i.e., alternatives of TBT- and TPhT-based antifoulants) after the Korean domestic and international regulations for TBT- or TPhT-based antifouling paints were established.

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