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Spatiotemporal distributions of butyltin compounds in various intertidal organisms along the Samcheok and Tongyeong coasts of Korea

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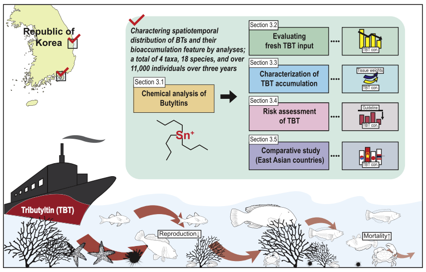
HIGHLIGHTS

- Butyltins (BTs) concentration differed in the two study areas and among species.
- Most intertidal organisms were less exposed to major concentrations of TBT.
- TBT accumulation was well correlated with the weight of the organisms.
- Fresh input of TBT was low in the study areas during the sampling period.
- Compared to other countries, concentrations of BTs were still greater in Korea.

GRAPHICAL ABSTRACT



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ABSTRACT

Thirteen years ago, the Korean Government introduced a regulation prohibiting the use of tributyltin (TBT), which was a component of antifouling paints. A subsequent decline in the concentration of butyltins (BTs) was recorded in seawater and the sediment, however, the current concentration of BTs in biota has not been well documented. The spatiotemporal distribution and concentration of BTs was recorded in biota from 2013 to 2015 along the coasts of Samcheok and Tongyeong using GS/MSD analysis. Crustaceans contained the greatest concentrations of BTs, followed by gastropods, fishes, and bivalves. We found that the concentration of BTs was greater at Tongyeong compared to Samcheok, because of the geographical characteristics of the area. We also confirmed that the regulation has been effective by showing that the TBT concentration decreased over the 3-year study period. The TBT levels of gastropods and bivalves fell within the limits of the guidelines and/or the effective concentration of the toxicological endpoint reported previously. The concentration of BTs also varied among species, being dependent on the weight of the soft tissue. Furthermore, the greater quantities of BTs degradation products compared to TBT confirmed the absence of recent inputs of pollutants during the study periods. However, compared with other Asian countries, biota BTs were greater in Korea, with noticeably greater concentrations along

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the south coast. Thus, further investigation of the distribution of BTs along the Korean coasts is required in the future. In conclusion, our results provide useful information about the recent trends of BTs in Korea.

1. Introduction

Butyltins (BTs) a component of hazardous chemicals that were first detected in the marine environment during the 1970s. Since the 1960s, these components have been widely used in pesticides and PVC preserved agents (Choi et al., 2009a). Tributyltin (TBT) is a type of butyltin that was mainly used in antifouling agents on fishing boats, vessels, and structures. Consequently, this chemical was released into the marine and fresh water environments, and negatively impacted the reproduction and development of marine organisms (Salazar and Salazar, 1991). For example, oyster exposed to TBT were subject to shell calcification (Waldock and Thain, 1983), while gastropods, such as *Reishia clavigera*, became infertile with females developing male organs (termed imposex) (Bryan and Gibbs, 1991). Because TBT is highly toxic, it also has major effects on the entire food chain, from phytoplankton to marine mammals (U'Ren, 1983; Bushong et al., 1988).

The accumulation of BTs depends on various factors. For instance, BTs negatively impacted the marine environment, with noticeably greater concentrations occurring along coastal areas near harbors and dockyards. BTs were also detected in semi-closed coastal areas where lower water circulation prevented the efficient flushing of this chemical. Affected areas included Ulsan, Masan, and Gohyun in Korea (Choi et al., 2009b). Biotic factors that impacted BTs accumulation included the size and age of organisms. Previous studies also reported significant correlations between biotic parameters and BTs accumulation (Choi et al., 2011, 2013a). Habitat type and the metabolism capability of biota also affect the extent to which BTs might accumulate (Lee, 1996; Jadhav et al., 2011).

Following confirmation of the harmful effects of BTs by many studies, the International Maritime Organization (IMO) adopted the ban in 2003. In Korea, the use of antifouling paints containing TBT was banned in March 2000 for small ships (<25 m), with the complete use of TBT being banned in November 2003 (Choi et al., 2010). However, most Asian countries have yet to implement such regulations.

Following the ban in the use of TBT in Korea, many studies have reported a decrease in BTs (Choi et al., 2013b; Kim et al., 2014). However, information about the recent trend in the distribution and concentration of BTs in Korea is lacking. Although several previous studies pointed out the species-specific accumulations of BTs in marine environment (Shim et al., 2005b; Jadhav et al., 2011), the bioaccumulation features of BTs cross varying taxa and/or within population have not been clearly examined until now. The present study analyzed a total of 4 taxa, 18 species, and over 11,000 individuals over three years, of which sufficient data provided a comprehensive understanding of bioaccumulation of BTs in coastal environment. The composition analysis and further calculations of BDIs provided the diagnosis on the recent input of TBT in the given areas. Thus, this study was designed to describe recent concentrations and occurrence of BTs in intertidal organisms to determine the effectiveness of regulations on TBT use in Korea. Then spatio-temporal trends and characterization of taxa containing BTs levels were analyzed. Comparison of our results with those of previous studies was expected to clarify the current status of BTs contamination in Korean coastal areas.

2. Materials and methods

This study aimed to determine the concentrations of BTs in various intertidal organisms, including gastropods (*Reishia clavigera*, Patellogastropoda sp., etc.), bivalves (*Mytilus galloprovincialis*, *Crassostrea gigas*), crustaceans (*Hemigrapsus sanguineus*, *Gaetice depressus*, etc.), fish (Gobiidae sp.), and ascidian (Pyuridae sp.). Of note, sedimentary BTs are out of scope in the present study.

2.1. Study area

Various intertidal organisms were collected from two coastal areas of Korea; namely, Samcheok (East coast) and Tongyeong (South coast) (Fig. 1). Sampling was conducted at three sites (S1–S3) in Samcheok from 2013 (November) to 2015 (December), and at three sites (T1–T3) in Tongyeong from 2013 (October) to 2015 (December). Samcheok is an exposed site located on the east coast of Korea (Fig. 1a). Despite the open sea enhancing its flushing efficiency with offshore waters, activities by military and coast guard ships affect this area. Military ships dock in the Sokcho and Uljin harbor near Samcheok (Lee et al., 2011). Thus, this area might be impacted by shipyard activity leading to the continuous accumulation of BTs. Tongyeong is located in the south coast of Korea, which represents the typical industrialized coastal region with semi-closed bay system. Accordingly, the bay experience relatively gentle seawater circulation with lack of flushing with offshore waters. Tongyeong Bay is one of the highly industrialized and urbanized areas in Korea, say numerous pollutants being released into the water and on the beach via various human activities such as neighboring industries and cities, shipyards, commercial fishing, and oyster farming etc. (Fig. 1b). Therefore, Tongyeong might be widely exposed to BTs pollution and other contaminants (Newton et al., 2014).

2.2. Sampling and sample preparation

Intertidal organisms, including gastropods ($n = 7134$), bivalves ($n = 2881$), crustaceans ($n = 605$), and fishes ($n = 200$), were collected form the intertidal zone at each sampling location over the 3 years (2013–2015). Details of the field study and species collected are shown in Tables S1 and S2 of the Supplementary Materials (S). The samples were immediately transported to the laboratory with dry ice. The shells of the bivalves, chitons, and gastropods were removed and whole somatic soft tissues were pooled and homogenized. The whole bodies of crabs and fishes were pooled and homogenized. Samples were stored at −20 °C and then freeze dried.

2.3. Analytical procedures

The analytical procedure was modified from that suggested by Shim et al. (1998) and Choi et al. (2009b). To analyze the samples, freeze dried samples (1 g) were extracted twice by mechanical shaking for 3 h with 20 mL of 0.1% tropolone-methylene chloride (Sigma Aldrich, Saint Louis, MO) and 10 mL of 6 N HCl (Sigma Aldrich) in 50 mL Teflon tubes. Diphenyltin dichloride was spiked in

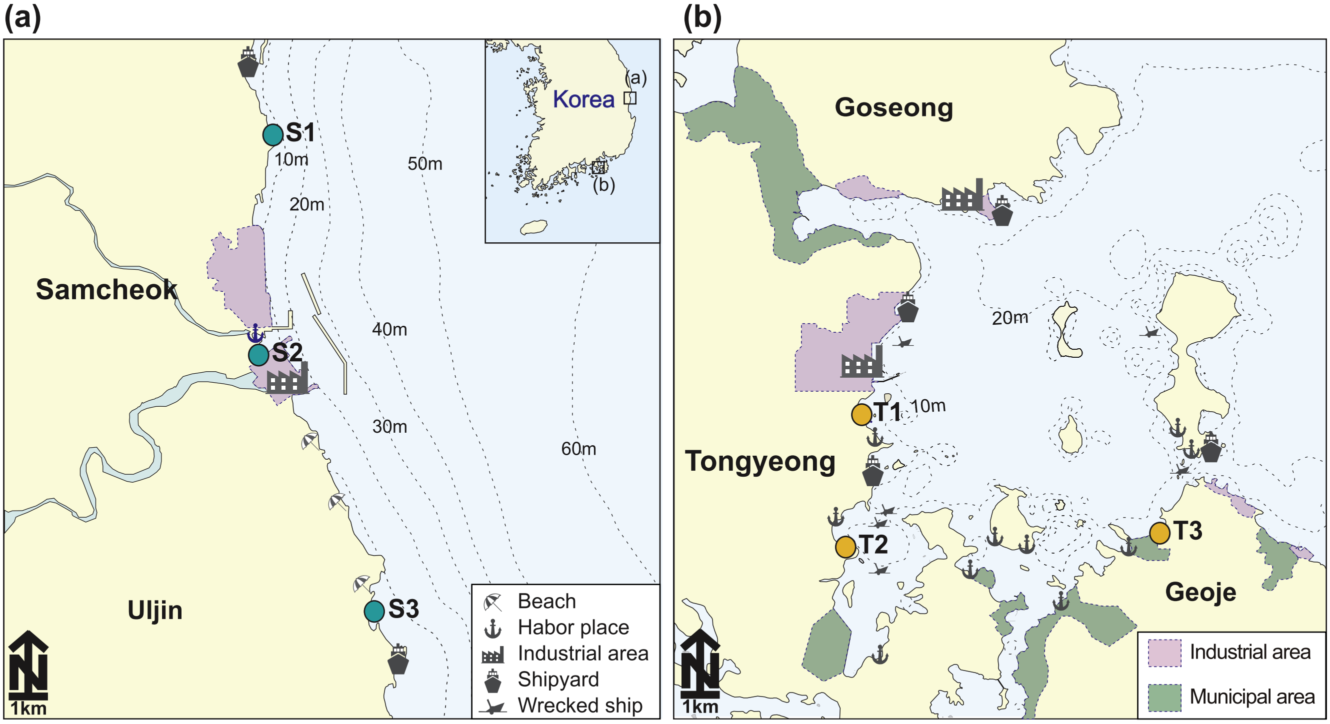


Fig. 1. Maps showing sampling sites at (a) Samcheok (S1–S3) and (b) Tonyeong (T1–T3), South Korea.

100 ng before extraction as a surrogate standard. After 10 min centrifugation (3000 rpm), 4 mL extracts were transferred to 15 mL glass test tubes and concentrated to approximately 200 μL. Then, the extract was transferred to hexane. The extract was hexylated with 500 μL Grignard reagent (Sigma Aldrich). The remaining Grignard reagent was removed with 10 mL of 1 N H_2SO_4 (Sigma Aldrich). The organic fraction was decanted, and the aqueous fraction was extracted with hexane and then cleaned by passing it through a Florisil column (Supelco, Bellefonte, PA) chromatograph. The eluents were concentrated to 1 mL under N_2. Finally, terphenyl-d14 (Supelco) was added as an internal standard.

2.4. Instrumental analysis

The methods used to identify and quantify BTs were previously described by Shim et al. (1998) and Choi et al. (2009b). GC/MSD instrumental conditions are summarized in Table S3. BTs concentrations were measured using an Agilent 7890 gas chromatograph (GC) coupled to a model 5975C mass-selective detector (MSD, Agilent technologies, Avondale, PA). A capillary column DB-5 (5% phenyl methyl siloxane, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness; J&W Scientific, Palo Alto, CA) was used. The GC temperature was programmed to 60 °C (2 min holding time) and heated to 300 °C (4 min holding time) at a rate of 10 °C/min. The injector and detector temperatures were maintained at 250 °C and 280 °C, respectively.

2.5. Quality control and statistical analysis

The accuracy of determining BTs concentration was checked by using certified reference materials (CE477 mussel tissue, European Commission) and their recovery at 85–116%, 97–115%, 74–92% for TBT, dibutyltin (DBT), and monobutyltin (MBT), respectively. BTs concentration was expressed as tin on a wet weight basis (ng Sn g^{-1} ww). The detection limits of BTs ranged from 1.4 to 3.1 ng Sn g^{-1} ww. Comparison of BTs concentrations between Samcheok and Tongyeong data was tested using Levene's test. We correlated soft tissue wet weight with amount of accumulated TBT (viz., content) and the relationship with each compound by using the Pearson correlation in SigmaPlot (Ver. 10, SPSS, Chicago, IL). Statistical significance was given as p values.

2.6. Calculating the butyltin degradation index (BDI)

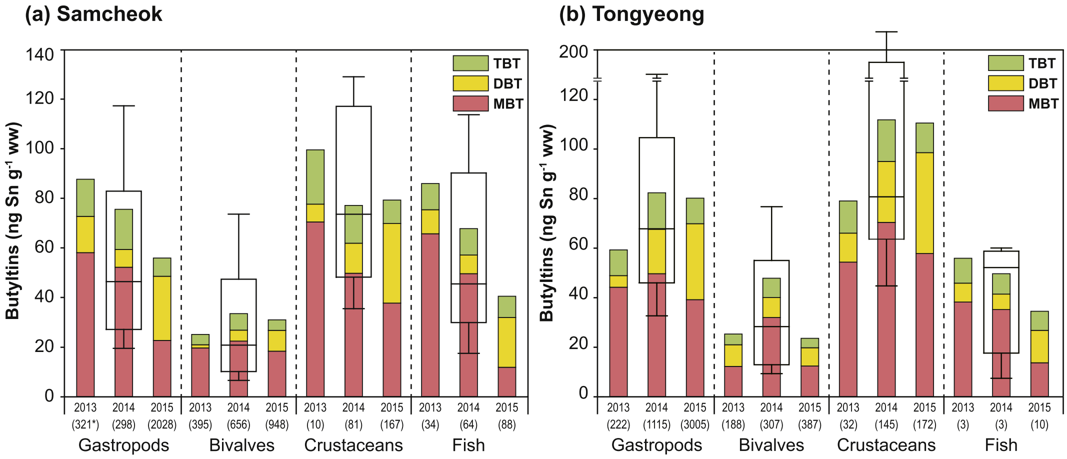
The BDI was calculated from the ratio between the breakdown products (DBT and MBT) with TBT. This index was calculated as Eq. (1):

$$\mathrm{BDI} = \frac{[\mathrm{MBT}] + [\mathrm{DBT}]}{[\mathrm{TBT}]} \tag{1}$$

3. Results and discussion

3.1. Distributions of butyltins in various intertidal organisms

BTs, including TBT and its breakdown products (DBT and MBT), were detected in all samples (Fig. 2 and Fig. S1). Thus, BTs are probably distributed throughout the intertidal areas of Samcheok and Tongyeong. TBT and DBT + MBT concentrations were significantly correlated ($p < 0.001$) in this study, indicating that DBT and MBT had primarily degraded from TBT (Hoch, 2001). Crustaceans contained the greatest concentration of BTs at both sites, ranging from 77 to 111 ng Sn g^{-1} ww. Considerably less concentration of BTs was found in gastropods (59–88 ng Sn g^{-1} ww) and fishes (34–86 ng Sn g^{-1} ww). Bivalves contained the least concentrations of BTs (23–48 ng Sn g^{-1} ww). These differences in BTs concentrations across species may be explained by the properties of BTs and the habitats used by the different species. In the marine environment, BTs have low solubility, mobility, and are easily adsorbed into



*Number of individuals experimented

Fig. 2. Temporal change and comparison between species in butyltins (BTs) concentrations observed in biota at (a) Samcheok and (b) Tonyeong from 2013 to 2015.

suspended particulate matter (SPM). Previous studies reported significant positive correlations between concentrations of BTs in sediments and organisms, which indicates direct uptake of suspended sediments followed by the bioaccumulation of BTs in coastal areas (Hwang et al., 1999; Nhan et al., 2005). And then, the deposition of BTs results in their assembling in the sediments. Consequently, BTs may be retained in the sediment for much longer years than in seawater (Hoch, 2001). For instance, previous studies reported that BTs levels tend to decrease in seawater, but not in sediment (Kim et al., 2014). Furthermore, crustaceans and gastropods are affected by sediment due to their burrowing habits and feeding type, whereas fishes and bivalves are more affected by seawater (Shim et al., 2005b; Jadhav et al., 2011; Choi et al., 2013b). Thus, difference in habitat use and feeding type, along with BTs characteristics, supports the observed higher concentrations of BTs in crustaceans and gastropods versus fishes and bivalves. Consequently, BTs characteristics and differences in habitat use of different species affect the body burden of this toxin in intertidal organisms.

Table 1 lists the intertidal organisms that were collected and the BTs concentrations documented from 2013 to 2015. Tongyeong had greater mean concentrations of BTs (83 ng Sn g^{-1} ww) compared to Samcheok (58 ng Sn g^{-1} ww) ($p < 0.026$) for the same species of organisms (except for samples collected just once during this study). This difference might be explained by the geographical features of the two study areas and the surrounding activities such as shipyards. For instance, Samcheok is open to the sea, whereas Tongyeong is a semi-enclosed bay (Fig. 1a). Thus, higher pollution loads might occur along the Tongyeong coast compared to the Samcheok coast, due to less flushing of water. Lee et al. (2011) demonstrated that geographical features influence BTs concentrations in Korea. The topography of the coast influences BTs concentrations, with the southern coastline being more complex than the eastern coastline (Fig. 1a). This feature acts as a barrier to the circulation of seawater, so pollutants form large ships that dock in the big harbors of Tongyeong might accumulate in this region. This bay also contains many beaches, ports, and shipwrecks, which may further enhance the effects of pollutants. This assumptions support a previous study stating that BTs contamination is higher in semi-closed bays with high shipping activity and poor water circulation when compared to open coastal bays (Hong et al., 2002). Meantime, it should be noted that Tongyeong and Samcheok might have continuing BTs sources from prevailing shipping activities around the coast, particularly Tongyeong has four large-scale shipyards around the coast (see Fig. 1). However, of note, TBT has been banned as use of antifouling agents since 2003 in Korea and lesser proportion of TBT compared to its degradation products such as DBT and MBT indicated lack of fresh BTs input in more recent years. Accordingly, paint chips commonly originated from shipyards, say one possible major source of TBT in the given area, may not be a major fresh sources in recent years. Thus, relatively great concentrations of BTs found in Tongyeong organisms might be attributable to the former exposure followed by the slow degradation of TBT containing paint chips in the given semi-closed bay system (Stang et al., 1992). Thus, our results confirm that the distribution of BTs contamination differs with coastal activities (Castro et al., 2012).

The TBT composition differed in the two study areas between 2013 and 2015. Biota contained TBT concentrations of 4–22 ng Sn g^{-1} ww in 2013 and 4–12 ng Sn g^{-1} ww in 2015. Compared with BTs levels in crustaceans between 2013 and 2015, TBT composition decreased from 20% to 12%. TBT levels also decreased in all other groups (gastropods: 18%–13%; bivalves: 17%–16%), except fishes (15%–22%). These declines in TBT indicate that there had been no recent fresh inputs of TBT in the two study areas, with the concentrations reflecting the degradation of past deposits (Stang and Seligman, 1986). Large quantities of DBT and MBT might be attributed to waste water and sewage disposal treatment from the industrial centers near to the study areas (Fent, 1996). Overall, the proportion TBT derived from BTs was much less for most species in 2015 compared 2013, suggesting no recent input of TBT.

3.2. *Comparison with ecotoxicological assessment criteria for TBT contamination*

To estimate whether the recent TBT inputs affect intertidal organisms, we investigated existing guidelines and used the cumulative probability distribution analysis. The TBT levels measured by our study (Samcheok and Tongyeong) were compared to ecotoxicological assessment criteria from other countries around the world. To compare the guidelines accurately, the species collected during our study were categorized according to phylum; namely, bivalves and gastropods. The guideline of the Public Works and Government service Canada (PWGSC, 2012) was 266 ng Sn g^{-1} dw, concentration, calculated assuming a moisture content of 80% (Stephen et al., 1985). This threshold was assumed to protect all organisms, including sensitive animals, such as gastropods. The Convention for the protection of the marine environment of the

Table 1
Summary of BTs concentration (ng Sn g^{-1} ww) across species from 2013 to 2015 in the two study areas.

Site	Classification	Species	n	TBT		DBT		MBT		∑BTs	
				Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean
Samcheok	Crustaceans	*Gaetice depressus*	57	4–10	8	nd-81	38	20–53	32	30–121	78
		Hemigrapsus sanguineus	178	4–34	13	nd-53	22	nd-120	43	31–152	79
		Pachygrapsus crassipes	21	12–18	15	7–14	11	23–102	74	47–141	99
	Gastropods	[a]*Chlorostoma lischkei*	26	6	–	18	–	38	–	62	–
		Littorina littorea	633	2–36	9	2–93	21	nd-94	30	8–152	60
		Monodonta labio	156	2–12	5	3–18	11	5–36	19	24–47	35
		Monodonta perplexa	364	3–13	6	4–57	30	nd-29	18	36–83	54
		Omphalius rusticus	60	2–9	6	13–51	27	8–33	19	23–75	52
		Reishia clavigera	120	4–15	9	7–18	13	nd-82	45	18–113	67
		Siphonaria japonica	126	3–64	29	3–33	18	nd-218	73	20–316	119
		Thylacodes adamsii	7	6–22	14	18–39	29	8–11	9	48–56	52
		Patellogastropoda sp.	1341	nd-47	11	nd-260	17	nd-205	39	7–284	67
	Fish	Gobiidae sp.	186	3–19	10	nd-63	14	nd-98	35	12–115	58
	Bivalve	*Mytilus galloprovincialis*	1999	nd-16	5	nd-41	6	nd-68	20	5–89	31
	Polyplacophora	[a]Chitonidae sp.	6	29	–	46		147	–	223	–
Tongyeong	Crustaceans	*Gaetice depressus*	76	6–21	13	31–66	45	nd-91	34	61–172	92
		Hemigrapsus sanguineus	272	4–30	14	6–113	30	nd-206	71	29–262	115
		[a]*Portunus trituberculatus*	1	15	–	8	–	11	–	35	–
	Gastropods	*Littorina littorea*	199	6–11	9	53–82	66	10–16	13	72–103	89
		Lunella correensis	1532	3–39	16	2–99	31	nd-153	56	33–184	103
		Monodonta labio	818	2–19	7	6–50	22	6–99	30	19–144	59
		Nerita japonica	185	5–13	8	41–104	63	11–32	18	56–149	89
		Omphalius rusticus	273	4–28	12	18–71	39	10–289	86	50–366	137
		Reishia bronni	56	5–22	13	26–84	55	9–86	47	40–192	116
		Reishia clavigera	1062	3–24	11	7–58	21	nd-119	41	33–160	73
		Thylacodes adamsii	84	6–23	12	4–81	22	4–82	39	40–133	73
		Patellogastropoda sp.	102	3–30	9	3–266	61	nd-45	20	6–318	91
	Fish	Gobiidae sp.	16	nd-14	8	3–23	10	4–147	55	8–161	74
	Bivalves	*Crassostrea gigas*	94	3–31	10	3–25	11	nd-71	27	15–92	47
		Mytilus galloprovincialis	788	nd-8	4	nd-21	7	nd-62	20	6–77	31
	Ascidian	Pyuridae sp.	136	4–21	9	nd-35	17	5–39	16	17–92	42
	Polyplacophora	Chitonidae sp.	490	3–38	16	3–69	24	nd-173	59	24–212	98

-: no available data.
[a] Samples collected just once during this study.

North-East Atlantic (OSPAR) commission suggested ecotoxicological assessment criteria (EAC) for TBT concentrations in mussels, which are used for bio-monitoring organisms. The upper EAC threshold was 71.7 ng Sn g^{-1} ww, which is expected not to cause acute toxic effects (Bignert et al., 2004) (Fig. 3). Oehlmann et al. (1996) reported that gastropods could become infertile by imposex at the value of 451 ng Sn g^{-1} dw.

Comparing the guidelines and endpoints proposed by previous

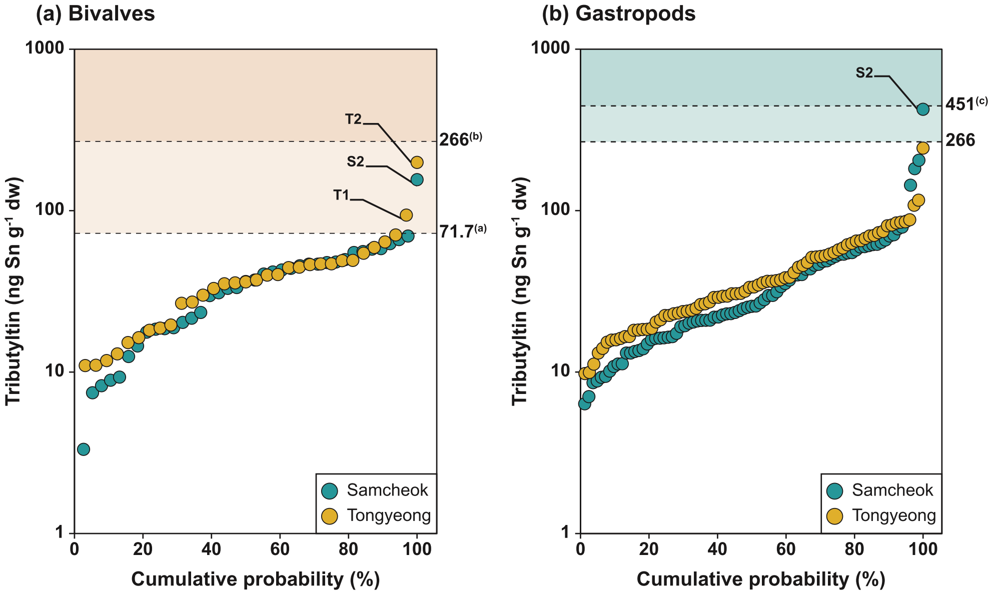


Fig. 3. Risk assessment by using cumulative probability distribution of TBT concentrations in (a) bivalves and (b) gastropods collected from Samcheok and Tonyeong (2013–2015) ([a] upper EAC of the OSPAR commission for mussels (Bignert et al., 2004); [b] lower threshold of the PWGSC guideline (PWGSC, 2012); and [c] sterilization concentrations due to imposex (Oehlmann et al., 1996)).

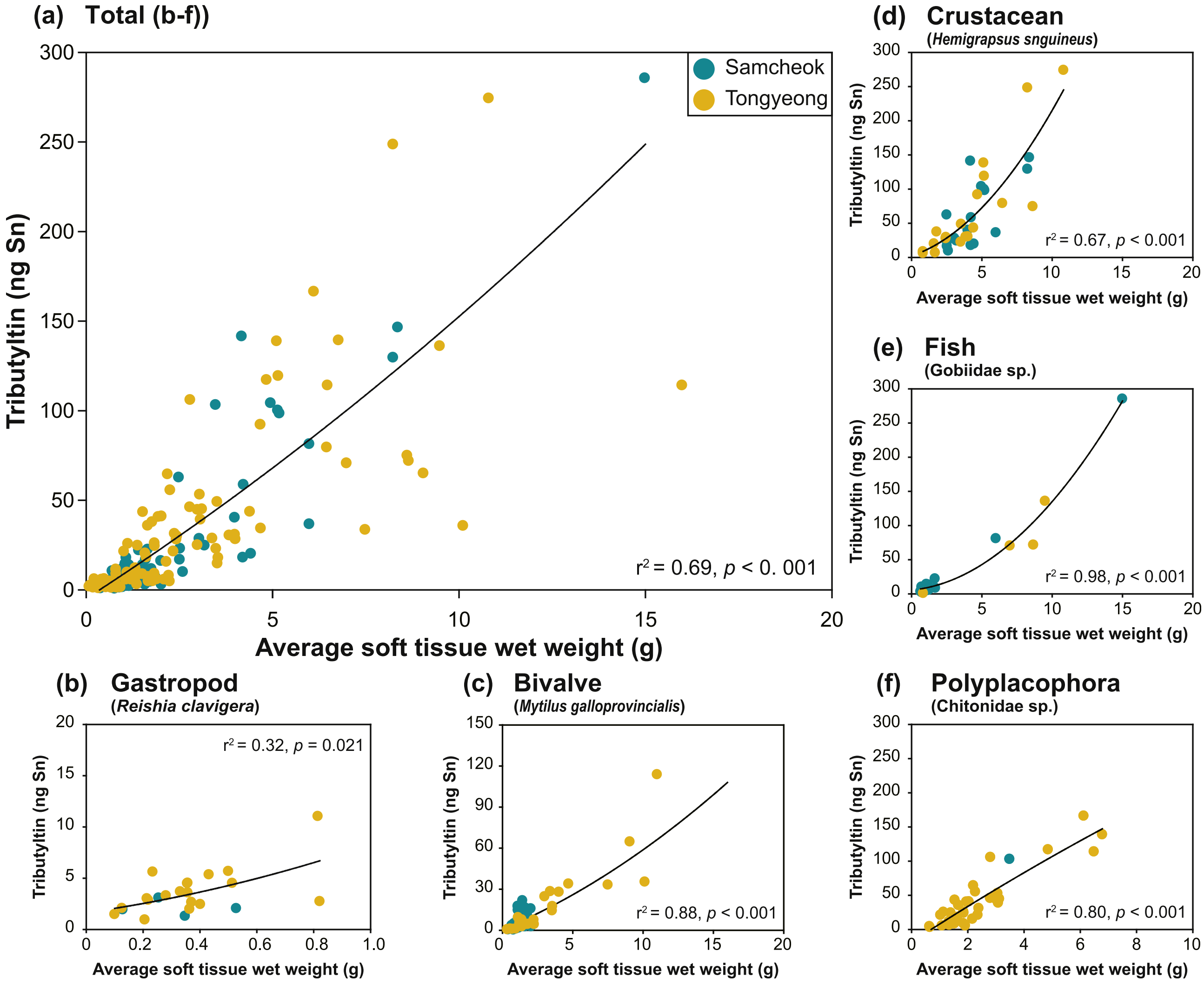


Fig. 4. Relationship between the TBT concentration and soft tissue wet weights in the species collected from the two study areas from 2013 to 2015. (a) Total, (b) gastropod, (c) bivalve, (d) crustacean, (e) fish and (f) polyplacophora in the study areas.

studies, we found that at least 90% of bivalves collected from our two study area between 2013 and 2015 did not exceed the upper EAC value. Less than 10% of bivalves exceeded this value; however, none of our bivalve samples exceeded the guideline proposed by the PWGSC (Fig. 3a). For gastropods, 100% of samples did not exceed the PWGSC value at Tongyeong. In contrast, one of the gastropods samples at S2 in Samcheok exceeded its value, but did not exceed the endpoint reported by Oehlmann et al., 1996 (Fig. 3b). Despite of the restriction of use in antifouling agents including TBT, the possible sources of TBT in the gastropod samples might come from the former TBT containing paint chips which had a long sustainability in ships' hull (Stang et al., 1992; Choi et al., 2009a). The concentrations of a few samples also exceeded the various thresholds. However, this result was not considered serious based on the guidelines. When compared to a previous study in Jinhae Bay (located near Tongyeong) from 1995/97 to 2012/13 (Kim et al., 2014), fewer samples exceeded the OSPAR guidelines in our current study. Overall, the TBT levels of most species met the safety criteria to protect marine life, with levels being much less compared to previous studies. Thus, the biota at Samcheok and Tongyeong might not have been exposed to major TBT pollution in recent years.

3.3. *Characterization of TBT accumulation*

To investigate characterization of TBT accumulation in each species, we compared the relationship between the soft tissue wet weight and the TBT concentration of each species collected at regular intervals in each sampling sites from 2013 to 2015 (Fig. 4). The relationship between TBT concentration and body weight also showed species-specific variation (Fig. 4b–f). In both the study areas, the amount of accumulated TBTs were positively correlated with individual biomass (Fig. 4a; $r^2 = 0.69$, $p < 0.001$). Looking by the group of taxa, the almost target organisms showed significant correlations ($p < 0.001$), either showing linear or exponential relationship. In anyhow, the result generally demonstrated the species-dependent bioaccumulation of TBT rather than site-specific bioaccumulation at this moment.

Previous studies reported that various biotic factors influence BTs accumulation, including, body weight, length, age, and sex. For instance, the extent of BTs accumulation in marine mammals is affected by their size and/or age. BTs accumulation might be associated with the balance of BTs uptake and excretion in animals (Choi et al., 2013a). Because immature mammals ingest greater quantities of BTs during feeding from surrounding environment,

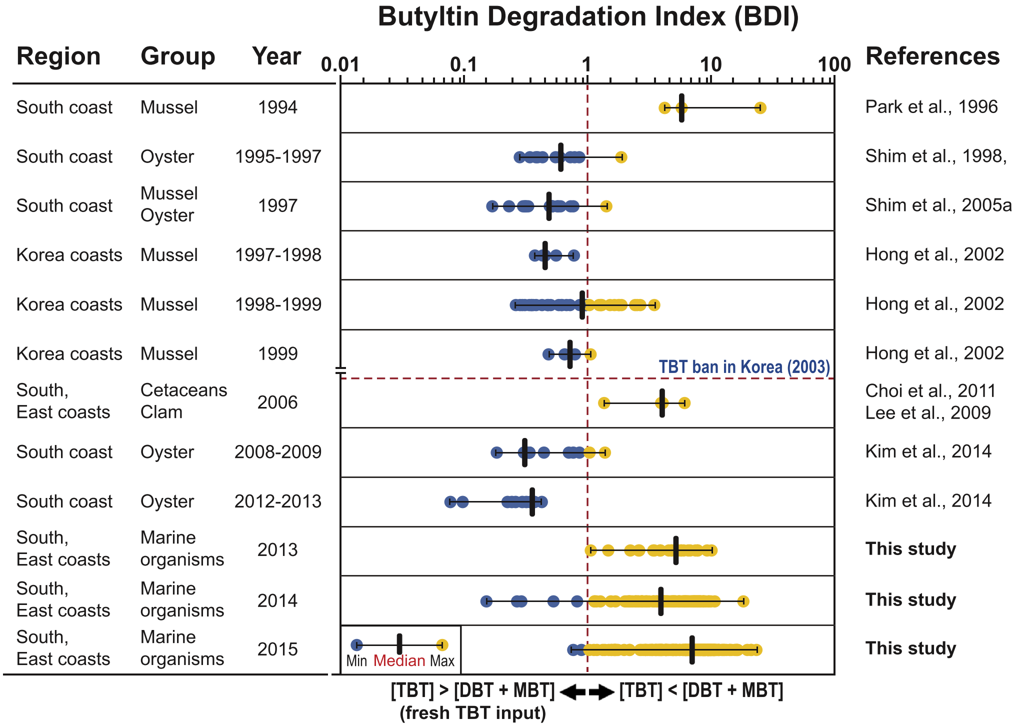


Fig. 5. Evaluating the effectiveness of TBT regulation in Korea by assessing butyltin degradation index (BDI) for previous and current studies conducted between 1994 and 2015.

with lower excretion rates, BTs accumulation increases relatively with age and size until maturity (Ciesielski et al., 2004). Stäb et al. (1996) also suggested that TBT concentrations decrease with increasing size for bivalves. Of note, the weaker correlation between the amounts of accumulated TBT versus growth proxy for gastropod, *Reishia clavigera* could be explained by their avoiding behavior in feeding strategy. Further environmental parameters being associated with TBT bioaccumulation would be necessary as many of biotic and abiotic factors could influence the degree and/or rate of TBT accumulation through (in)direct uptake from water or sediment and dietary uptake in combined manner (Lee, 1996; Kono et al., 2008).

For instance, differences in the metabolism of BTs in each species affect BTs accumulation. TBT enters organisms and is metabolized by certain reactions. The first reaction involves the cytochrome P-450 dependent monooxygenase system, which hydroxylates TBT to its derivatives. The second reaction conjugates sugars or sulfate to hydroxybutyldibutyltin, after which these compounds are rapidly removed. Fishes and crustaceans have active P-450, which eliminates TBT easily. In contrast, mollusks (gastropods and bivalves) have low quantities of P-450, resulting in their having difficulty removing TBT, resulting in low rates of TBT metabolism (Lee, 1996).

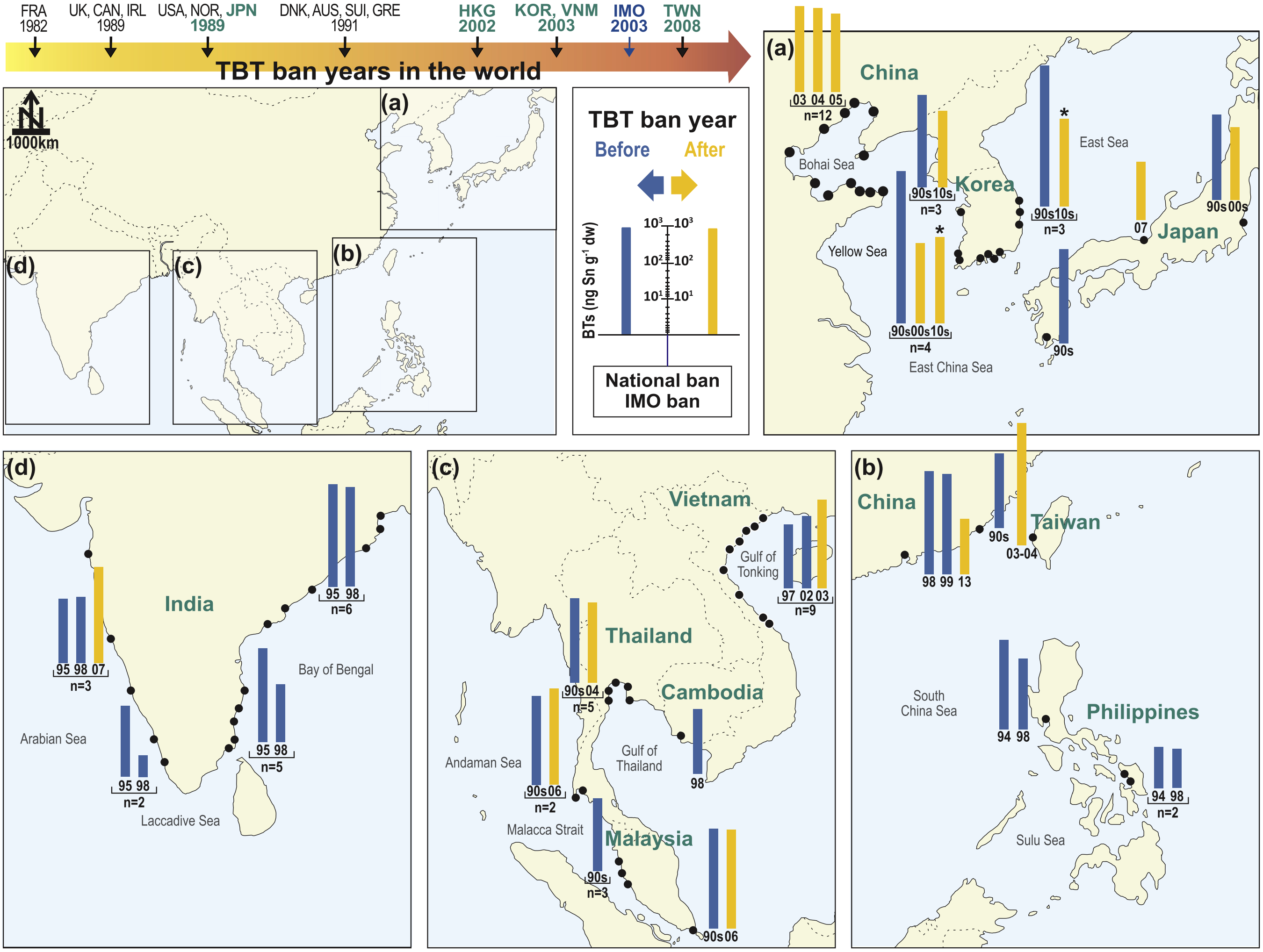
Although the cytochrome P-450 in certain marine organisms would metabolize TBT compound (Lee, 1996), continuing exposure of TBT from the environment might hinder their metabolizing capacity or excretion ability (Shim et al., 2000; Kim et al., 2008). Apart from the BT's physicochemical properties, various environmental condition would influence the BTs bioaccumulation. For example, *Reishia clavigera* aggregates in clefts during the winter season and do not feed up to ~5 months, which gives more chances to biodilution and/or excretion of TBT over the life span (Skarphédinsdóttir et al., 1996). Even though fishes and crustacean have active P-450, sustained exposure of TBT from the environment could cause excessive bioaccumulation of TBT as they grew.

Overall, our results showed that the quantity of TBT in marine organisms was dependent on various biotic and abiotic factors (Sections 3.2 and 3.3), including 1) habitat, 2) body weight, and 3) metabolism rate of TBT by each organisms. Thus, these factors might also affect the rate of BTs accumulation. Consequently, TBT accumulation might differ across species (Harino et al., 2000, 2002). In contrast to Choi et al. (2013b), other studies reported no significant correlation between biotic factors and TBT concentrations (Harino et al., 2000; Ohji et al., 2006). Thus, more comprehensive studies on TBT concentrations in marine organisms and the interactions between factors are needed.

3.4. Changes to the butyltin degradation index

TBT is widely used as an additive in antifouling products. However, it cannot be easily degraded in marine environment, requiring two times longer compared to bivalves and four times longer compared to seawater. Choi et al. (2009b) demonstrated the half-lives of TBT in seawater (0.78 year), sediment (2.89 year), and bivalves (1.12 year). When TBT is released into the marine environment from certain sources, it is degraded to breakdown products, such as DBT and MBT (Kim et al., 2008). However, the input of fresh TBT results in its residues being continuously maintained in the marine environment. To predict whether the input of fresh TBT is recent, we calculated the butyltin degradation index (BDI), which indicates the degree of TBT degradation (Fig. 5). BDI could be determined by calculating the ratio between the concentration of TBT and that of DBT + MBT. If the calculated BDI value is below 1 for the BTs levels of marine organisms, recent input of TBT to the marine environment where the biota live is predicted. However, if the BDI value exceeds 1, no new input is indicated (Dıez et al., 2002).

The BDI obtained for BTs in various biota by previous studies and our study between 1994 and 2015 is shown in Fig. 5. BDI ranged from 4 to 25 in Kwangyang Bay in 1994, indicating no fresh input of



*Kim et al. 2014 and this study

Fig. 6. Comparisons of BTs concentrations in biota collected from the coastal waters of East Asian countries. Concentration of BTs in each countries also is shown in Table S5.

TBT (Park et al., 1997). From 1995 to 1997, BDI from 12 samples of bivalves ranged from 0.2 to 1.8, and did not exceed 1 for 91% of the samples ($n = 12$) (Shim et al., 1998, 2005a). Studies along the Korean coasts from 1997 to 1999 indicated that 50% of samples ($n = 94$) had a BDI of less than 1 (Hong et al., 2002; Shim et al., 2005b). After the regulation against the use of TBT was implemented in November 2003 in Korea, the BDI index changed. Lee et al. (2011) and Choi et al. (2011) showed that the BDI of samples from the south and east coasts of Korea exceeded 1, indicating no fresh input. BDI ranged from 0.1 to 23.6 from 2013 to 2015, with the BDI exceeding 1 for 92% of samples ($n = 497$) collected by Kim et al. (2014) and the current study. The BDI for the Samcheok and Tongyeong coasts was high, indicating low TBT input from pollutants in recent years. Thus, our results indicate that TBT regulation might have been effective at decreasing TBT concentrations (Kim et al., 2014).

3.5. Status of BTs contamination in marine organisms across countries in East Asia

TBT residues in the marine environment affect various marine organisms. For instance TBT exposure causes reduced growth in mollusks (Salazar and Salazar, 1991), shell calcification in oysters (Alzieu, 1996), and infertility by imposex in gastropods (Bryan and Gibbs, 1991). Furthermore, the breakdown products (such as DBT and MBT) negatively affect blood cells and cause immunosuppression in marine animals (Kobayashi et al., 1996; Bouchard et al., 1999). Because of theses harmful effects, there was a strong movement to ban the use of TBT globally (Arai and Harino, 2009). However, in East Asia, only Japan (1989), Hong Kong (1992), Korea (2003), Vietnam (2003), and Taiwan (2003) have banned TBT use.

Previous studies have demonstrated widespread BTs contamination across East Asia. The distribution of BTs before and after the TBT ban was legislated in each country or IMO is shown in Fig. 6 and Table S4. We assimilated the data from previous studies to calculate the average BTs concentrations in the areas adjacent to each country. BTs concentration decreased with time in India during the 1990s. However, the distributions of BTs increased in the 2000s in certain locations within the country (Goa, Karwar, Mumbai) (Kan-Atireklap et al., 1998; Sudaryanto et al., 2002; Jadhav et al., 2011). Because India is one of the most rapidly developing countries in Asia, BTs concentrations might have further increased in recent years. China has no legislation against the use of TBT, however, BTs concentrations in mollusks decreased from 2003 to 2005 along the Bohai coast (Yang et al., 2006, 2008). Furthermore, because the Hong Kong is working to control the use of TBT, BTs levels along the coasts of Hong Kong have also declined in recent years compared to the 1990s (Sudaryanto et al., 2002; Deng et al., 2015). Malaysia, Cambodia, and the Philippines have no BTs regulations, with BTs concentrations remaining similar or increasing compared to past levels (Sudaryanto et al., 2002, 2004), reflecting their growing industrial activities and trade (Arai and Harino, 2009).

Japan was the first country to ban the use of TBT in Asia, with many pre and post TBT ban studies. The regulation was introduced in 1989, and was so effective that BTs concentrations decreased in Otsuchi Bay (Harino et al., 2003, 2007) to levels that were less than those documented in Taiwan and other countries in recent years (Tang and Wang, 2009; Chen et al., 2016). Korea banned the use of TBT in 2003, with this regulation proving highly effective. Studies showed that BTs concentrations were high during the 1990s along the coasts of Korea coasts. However, after the regulation was implemented in 2003, BTs levels were less in the 2000s and 2010s compared to the 1990s (Lee, 2009; Choi et al., 2013a; Kim et al., 2014).

Many studies have investigated the concentrations of BTs in sediment and seawater; however, few studies have investigated BTs concentrations in biota, particularly in Korea. Our results show that many marine organisms continue to suffer from BTs contamination. Because BTs accumulate in biota along the food chain, marine organisms at higher trophic levels are probably more susceptible to BTs. Thus, it is important to investigate BTs accumulation in various organisms across the food web (Ho and Leung, 2014). The current study investigated BTs contamination in the coastal area of Korea (Samcheok and Tongyeong). Crustaceans showed the greatest concentration of BTs while bivalves contained the least concentration at both study areas indicating species-specific BTs distribution. And the concentration of BTs observed in biota in Tongyeong was greater than in Samcheok due to difference of the geographical feature. We found low BTs levels in the various marine organisms that were sampled, with levels meeting various guidelines (i.e., below thresholds considered to cause harmful effects). We found that TBT concentration was correlated with wet tissue weight, with evident BTs accumulation in biota. And, we detected low levels of fresh TBT input, obtaining high BDIs in according to decreased TBT levels because of the ban or its degradation. Furthermore, BTs levels in the coastal areas of Korea were similar or higher compared to those recorded in other countries in Asia, with a clear increase along the south coast of Korea. Thus, systematic post-monitoring of the distribution of BTs along the coasts of Korea is recommended.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.12.152.

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<Supplementary Materials>

Spatiotemporal distribution of butyltin compounds in various intertidal organisms along the Samcheok and Tongyeong coasts of Korea

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Supplementary Figures

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Supplementary Tables

Table S1. Details of the field study, summarized for Datasets I to III.

		Data set I (2013)	Data Set II (2014)	Data Set III (2015)
Samples from:		Biota	Biota	Biota
Number of Samples	Gastropods	543	1,832	5,126
	Bivalves	583	963	1,335
	Crustaceans	42	226	350
	Fishes	37	67	98
Number of species classification	Gastropods	4	7	12
	Bivalves	2	2	2
	Crustaceans	1	4	3
	Fishes	1	1	1
Key parameters		MBT, DBT, TBT	MBT, DBT, TBT	MBT, DBT, TBT
Sampling locations		S1, S2, S3 T1, T2, T3	S1, S2, S3 T1, T2, T3	S1, S2, S3 T1, T2, T3

Table S2. Summary of the marine organisms, sampling sites, and years of study.

Site	Area description	Species	n	Sampling year	Classification
Samcheok					
S1	Bihwa Port	Gobiidae sp.	70	2013-2015	Fish
		Patellogastropoda sp.	435	2013-2015	Gastropod
		Mytilus galloprovincialis	730	2013-2015	Bivalve
		Hemigrapsus sanguineus	119	2013-2014	Crustacean
		Monodonta labio	156	2014	Gastropod
		Thylacodes adamsii	7	2014/2015	Gastropod
		Gaetice depressus	57	2015	Crustacean
		Chlorostoma lischkei	26	2015	Gastropod
		Littorina littorea	51	2015	Gastropod
		Monodonta perplexa	246	2015	Gastropod
		Omphalius rusticus	39	2015	Gastropod
		Chitonidae sp.	6	2015	Polyplacophora
S2	Hosan Port	Gobiidae sp.	24	2013-2014	Fish
		Hemigrapsus sanguineus	57	2013-2014	Crustacean
		Mytilus galloprovincialis	719	2013-2015	Bivalve
		Patellogastropoda sp.	466	2013-2015	Gastropod
		Reishia clavigera	103	2014-2015	Gastropod
		Pachygrapsus crassipes	17	2014-2015	Crustacean
		Littorina littorea	253	2015	Gastropod
		Monodonta perplexa	88	2015	Gastropod
		Omphalius rusticus	21	2015	Gastropod
		Siphonaria japonica	25	2015	Gastropod
S3	Nagok Beach	Gobiidae sp.	92	2013-2015	Fish
		Mytilus galloprovincialis	550	2013-2014	Bivalve
		Littorina littorea	192	2013-2014	Gastropod
		Patellogastropoda sp.	440	2013-2014	Gastropod
		Reishia clavigera	19	2015	Gastropod
		Hemigrapsus sanguineus	2	2015	Crustacean
		Pachygrapsus crassipes	4	2015	Crustacean
		Monodonta perplexa	30	2015	Gastropod
		Siphonaria japonica	50	2015	Gastropod

Table S2. (*Continued*)

Site	Area description	Species	n	Sampling year	Classification
Tongyeong					
T1	Near Industrial area	*Hemigrapsus sanguineus*	127	2013-2015	Crustacean
		Chitonidae sp.	176	2013-2015	Gastropod
		Crassostrea gigas	6	2014-2015	Bivalve
		Mytilus galloprovincialis	96	2014-2015	Bivalve
		Reishia clavigera	351	2014-2015	Gastropod
		Lunella correensis	474	2014-2015	Gastropod
		Monodonta labio	310	2014-2015	Gastropod
		Pyuridae sp.	128	2014-2015	Ascidian
		Reishia bronni	42	2015	Gastropod
		Gobiidae sp.	9	2015	Fish
		Gaetice depressus	29	2015	Crustacean
		Heminerita japonica	72	2015	Gastropod
		Littorina littorea	35	2015	Gastropod
		Omphalius rusticus	32	2015	Gastropod
		Thylacodes adamsii	14	2015	Gastropod
		Patellogastropoda sp.	19	2015	Gastropod
T2	In front of Sonduck Village	Gobiidae sp.	5	2013-2015	Fish
		Crassostrea gigas	37	2013-2015	Bivalve
		Mytilus galloprovincialis	205	2013-2015	Bivalve
		Hemigrapsus sanguineus	129	2013-2015	Crustacean
		Lunella correensis	957	2013-2015	Gastropod
		Thylacodes adamsii	41	2013-2015	Gastropod
		Portunus trituberculatus	1	2014	Crustacean
		Reishia clavigera	68	2014	Gastropod
		Monodonta labio	282	2014-2015	Gastropod
		Chitonidae sp.	115	2014-2015	Polyplacophora
		Gaetice depressus	8	2015	Crustacean
		Littorina littorea	164	2015	Gastropod
		Omphalius rusticus	107	2015	Gastropod
		Reishia bronni	14	2015	Gastropod
		Patellogastropoda sp.	20	2015	Gastropod
T3	Near Sadeung Elementary School	*Mytilus galloprovincialis*	487	2013-2015	Bivalve
		Gaetice depressus	39	2014	Crustacean
		Crassostrea gigas	51	2014-2015	Bivalve
		Reishia clavigera	643	2014-2015	Gastropod
		Lunella correensis	101	2014-2015	Gastropod
		Monodonta labio	226	2014-2015	Gastropod
		Chitonidae sp.	199	2014-2015	Polyplacophora
		Patellogastropoda sp.	63	2014-2015	Gastropod
		Pyuridae sp.	8	2015	Ascidian
		Hemigrapsus sanguineus	16	2015	Crustacean
		Heminerita japonica	113	2015	Gastropod
		Omphalius rusticus	134	2015	Gastropod
		Thylacodes adamsii	29	2015	Gastropod

Table S3. GC/MSD instrumental conditions for determining butyltins compounds.

GC/MSD system	Agilent 7890A GC and 5975C MSD
Column	DB-5MS (30 m long, 0.25 mm i.d., 0.25 μm film thickness)
Gas flow	1 mL/min He
Injection mode	Split \less
Injector temperature	300 °C
Injection volume	2 μL
Column flow	1.0 ml min^{-1}
Ionization	EI mode (70 eV)
MS temperature	180 °C
Detector temperature	230 °C
Oven temperature	60 °C hold 2 min Increase 6 °C/min to 300 °C 300 °C hold 4 min
Target BTs	Tributyltins, Dibutlytin, Monobutyltin

Table S4. Physicochemical properties of targeted butyltin compounds.

Physicochemical properties[a]	Butyltin compounds TBT	 DBT	 MBT
Molecular weight	325.508 g mol^{-1}	303.842 g mol^{-1}	282.176 g mol^{-1}
Boiling point	140 °C (13 hPa)	148 °C (16 hPa)	93 °C (13 hPa)
Melting point	-9 °C	37 – 38 °C	-63 °C
Solubility	0.017 g / L	0.32 g / L	N/A (immiscible)
Log K_{ow}	4.76	0.97	0.41

[a] Pub-chem open chemistry database; N/A: no data available

Table S5. Comparison of tributyltin (TBT) concentrations in the biota collected from the coastal areas of East Asia.

Country	Site	TBT ban year	Sampling date	Organism	Butyltins(a)				BDI	References
					MBT	DBT	TBT	∑BTs		
Korea		2003								
	Kwangyang		1994	Bivalves	6-21	3-18	1.2-2.2	11-30	1-9.6	Park et al. 1996
	Jinhae Bay		1994		nd	14.1	nd	14.1	nd	
	Coast area		1997	Starfish	nd-572	2-150	nd-27	12-1035	1.6-104.6	Shim et al. 2005a
				Bivalves	nd-92	5-140	3-322	8-493	0.2-1.4	
	South coast		1997-1998	Bivalves	6-216	9-566	7-492	25-1233	0.4-3.5	Hong et al. 2002*
	East coast		1998		10-203	18-334	23-111	51-648	0.4-4.9	
	West coast		1998		2-5	7-22	5-16	15-425	1.7-2.2	
	Coast area		1995-1998	Bivalves	24	34	113	172	0.5	Shim et al. 2005b
			2001		19	53	98	170	0.7	
	Coast area		2000	Gastropods	-	-	1-102	-	-	Shim et al. 2000
	Coast area		2001-2003	Bivalves	-	-	2-516	-	-	Choi et al. 2009*
			2004-2005		-	-	nd-63	-	-	
	Coast area		2004/2009	Gastropods	nd	nd-29	nd-37	nd-66	-	Choi et al. 2013
	Coast area		2006	Cetaceans	82-26	30-151	12-141	53-247	0.3-9.6	Choi et al. 2011
	West, South		2006	Bivalves	nd	nd	nd-60.2	nd-60.2	-	Lee et al. 2009
	Jinhae Bay		2008-2009	Bivalves	nd-7.2	2-22	10-69	15-86	0.2-1.1	Kim et al. 2014
			2012-2013	Bivalves	nd-9	nd-14	6-92	7-125	0-1.5	
	East, South		2013-2015	Marine organisms	nd-394	nd-266	nd-64.3	5-430	nd-48.4	**This study**
China		-								
	Finless porpoise		1990-1991	Cetaceans	34	193	34	261	6.7	Tanabe et al. 1998*
	Pearl River		1998	Bivalves	1	48	13	63	4	Zhang et al. 2002
				Fishes	nd	6.2-15.2	5-19	11-34	0.8-1.6	
				Shrimp	0.6	12.2	3.6	16.4	3.6	
	Hong Kong coast area	1992	1999	Bivalves	3-63	3-39	7-135	15-234	0-2	Sudaryanto et al. 2002*
	Bohai coast		2002	Mollusks	nd-52.2	nd-358	nd-383	nd-407	nd-16	Yang et al. 2004
			2004-2005		3-18	7-39	4-67	15-97	0.4-3.9	Yang et al. 2008
	Coast area		2004	Gastropods	nd-140	nd-39	nd-7	nd-182	nd-53.8	Leung et al. 2006
	Dapeng Bay Daya Bay		2012	Gastropods	-	1-7	1-49	-	-	Ho and Leung 2014
	Futian		2013	Gastropods	-	11-2	nd-5	-	-	Deng et al. 2015
				Bivalves	-	2	1	-	-	
				Fishes	-	nd-3	nd-2	-	-	

Table S5. (*Continued*)

Country	Site	TBT ban year	Sampling date	Organism	Butyltins(a)				BDI	References
					MBT	DBT	TBT	∑BTs		
Japan		1989								
	Coast area		1981-1997	Cetaceans	240	1154	260	1654	5.3	Tanabe et al. 1998*
			1990/1995	Pinnipeds	31	31	17	79	4	
	Tokyo Bay		1989	Bivalves	14-81	21-2778	8-98	142	3.3	Higashiyama et al. 1991*
	Osaka		1989	Bivalves	nd	nd	10-12	-	-	Harino et al. 1999*
			1990-1996		nd	nd	2-115	-	-	
	Coast area		1990-1991	Gastropods	nd	nd	nd-205	-	-	Horiguchi et al. 1997*
	Otsuchi Bay		1994-2001	Shrimp	nd-12	nd-8	1.4-35	1.4-45	nd-1.8	Takeuchi et al. 2004*
	Ostuchi Bay		1995-1999	Bivalves	7-21	7-24	21-59	35-102	0.7-1.2	Harino et al. 2003
			2005	Bivalves	0.8-6	0.6-18	0.6-57	2-82	0.4-2.7	Harino et al. 2007
	Northern Kysushu		1998-2001	Bivalves	-	-	8-42	-	-	Inoue et al. 2006*
	Maizuru Bay		2003	Bivalves	0.83-2.9	0.83-3.1	0.77-11	-	-	Ohji et al. 2007
			2007	Bivalves	2-4	1-4	2-9	6-17	0.8-1.8	Eguchi et al. 2010
	Koshima Bay		2005	Bivalves	25-107	5-38	2-114	49-259	1-28	Koyama et al. 2012*
				Gastropods	23-188	5-34	1-42	29-253	5.1-173.4	
India		-								
	Coast area		1994	Bivalves	nd-250	nd-110	nd-150	2-378	0-25	Kan et al. 1997
	Coast area		1998	Bivalves	nd-45	nd-77	nd-233	nd-343	0-30	Sudaryanto et al. 2002*
	Goa		2007	Bivalves	18-34	32-55	104-168	154-257	0.5-0.5	Jadhav et al. 2011
	Karwar				9-37	47-91	56-67	120-188	0.9-2.3	
	Mumbai				6-17	2-9	23-27	34-60	0.4-1.6	
Taiwan		2008								
	Luermen stream estuary		2003-2004	Bivalves	3-6907	21.9-6160	86.2-5770	139-18837	0.1-2.3	Tang et al. 2009
	Kaohsiung harbor		2006	Brachyura (muscle)	0.2-15	2-54	2-82	9-939	0.4-2.9	Chen et al. 2016
				Brachyura (crab hepatopancreas)	7-298	15-288	25-352	50-939	0.6-6.3	
Vietnam		2003								
	Coast area		1998	Bivalves	nd-2	nd-10	1-34	1-44	0-2	Sudaryanto et al. 2002*
	Coast area		2002	Bivalves	0.2-6	0.1-1.2	0.3-9.4	0.8-11	0.2-16.1	Midorkawa et al. 2004
	Coast area		2003	Bivalves	0.6-4	0.8-5	0.8-3	2-12	1.9-3	Nhan et al. 2005

Table S5. (*Continued*)

Country	Site	TBT ban year	Sampling date	Organism	Butyltins(a)				BDI	References
					MBT	DBT	TBT	∑BTs		
Malaysia		-								
	Coast area		1997-1998	Fishes	2-7	nd-13	2.4-190	5.3-210	0.1-2.3	Sudaryanto et al. 2004
	Coast area		1998	Bivalves	nd-50	nd-82	1-299	1-426	0-2	Sudaryanto et al. 2002*
Cambodia		-								
	Coast area		1998	Bivalves	nd-17	nd-19	1-36	1-72	0-12	Sudaryanto et al. 2002*
Philippines		-								
	Coast area		1997-1998	Bivalves	nd-10	nd-10	nd-19	nd-34	nd-5	Sudaryanto et al. 2002*

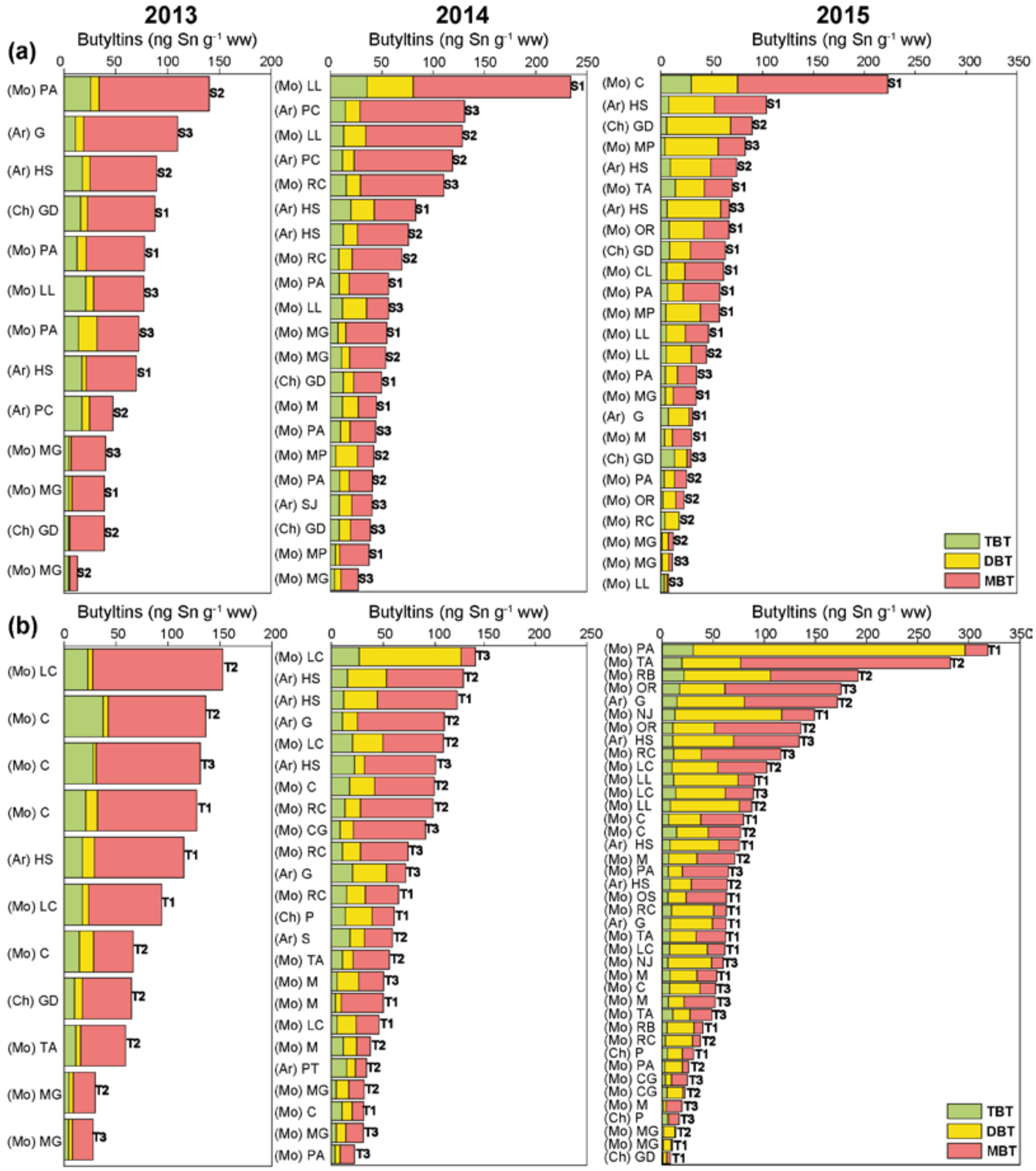
nd: not detected, -: no data available

*Concentrations were normalized to Sn ion.

(a) Concentration was calculated assuming a moisture content of 80%, except for this study (Stephen et al., 1985).

Stephen, C.E., Mount, D.I., Hansen, D.J., Gentile, J.R., Chapman, G.A., Brungs, W.A., 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. US EPA Report, PB-85-227049, National Technical Information Service, Springfield, VA, USA.

Supplementary Figures



Mo: Mollusca Ch; Chordata Ar; Arthropoda
C: Chitonidae sp.; CL: *Chlorostoma lischkei*; CG: *Crassostrea gigas*; G: *Gaetice depressus*; GD: Gobiidae sp.;
HS: *Hemigrapsus sanguineus*; NJ: *Nerita japonica*; LB: *Littorina littorea*; M: *Monodonta labio*; MP: *Monodonta perplexa*;
MG: *Mytilus galloprovincialis*; OR: *Omphalius rusticus*; PA: Patellogastropoda sp.; PC: *Pachygrapsus crassipes*;
PT: *Portunus trituberculatus*; P: Pyuridae sp.; RB: *Reishia bronni*; RC: *Reishia clavigera*; TA: *Thylacodes adamsii*;
SJ: *Siphonaria japonica*; LC: *Lunella coreensis*

Fig. S1 Spatiotemporal distribution of Butyltin in the intertidal organisms at (a) Samcheok (S1-S3) and (b) Tongyeong (T1-T3). Species sampeld were classfied according to Phylum.

Fig. S1. Spatiotemporal distributions of butyltin in the intertidal organisms at (a) Samcheok (S1-S3) and (b) Tongyeong (T1-T3).