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Three decades of TBT contamination in sediments around a large scale shipyard

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ABSTRACT

Tributyltin (TBT) contamination in sediments was investigated in the vicinity of a large-scale shipyard in the years after the implementation of a total ban on the use of TBT based antifouling paints in Korea. Extremely high level of TBT (36,292 ng Sn/g) in surface sediment was found at a station in front of a dry-dock and near surface runoff outfall of the shipyard. TBT concentration in surface sediments of Gohyeon Bay, where the shipyard is located, showed an apparent decreased TBT concentration gradient from the shipyard towards the outer bay. The vertical distribution of TBT contamination derived from a sediment core analysis demonstrated a significant positive correlation ($r^2 = 0.88$; $p < 0.001$) with the annual tonnage of ship-construction in the shipyard within the past three decades. TBT concentrations at six stations surveyed before (2003) and seven years after (2010) the total ban showed no significant differences ($p > 0.05$). Despite the ban on the use of TBT, including ocean going vessels, surface sediments are still being heavily contaminated with TBT, and its levels well exceeded the sediment quality guideline or screening values.

1. Introduction

Tributyltin (TBT), one of the organotin compounds, has been actively used as biocidal additives to restrain the adhesion of marine organisms in large ships, fishing boats, and harbor structures since 1960 [1]. This major application of TBT to ship hulls eventually releases the chemical to the surrounding marine environment, contaminating water, sediment and marine biota. Since early 1980s toxic effects of TBT, on marine organisms have been recognized [2]. Thus, the use of TBT antifouling agent has been regulated in many countries [3,4]. The Anti-Fouling System (AFS) Treaty of International Maritime Organization's (IMO) ban on new application of TBT based antifouling paints [5] has entered into force since 2008. Before IMO AFS treaty, most countries have regulated the use of TBT in small ships of less than 25 m in length. The use of TBT has been regulated in Korea since 2000 gradually, and it was totally banned, including in ocean going vessels, from November 2003 [6]. In spite of that, high concentrations of TBT in sediments have been observed in places where heavy shipping and ship-building activities exist [7–9] even long after the ban of TBT.

Many of TBT monitoring in marine sediments were conducted in coastal areas including marinas, harbors, shipyards, anchorage and shipping tracks [3,10–12]. Thus, a shipyard is a localized TBT point source [13], yet there is limited information on TBT contamination in the vicinity of large shipyards where new ships are built and maintained regularly [7,14–16]. A ship with a newly applied antifouling paint generally shows high initial leaching of TBT from the ship hulls. Additionally, over spraying of antifouling paint in dry-dock and painting facility releases TBT to surrounding environment. Further, when a shipyard discharges untreated effluents to sea, considerable amount of TBT enters the surrounding waters [5]. When a total ban on new application of TBT to ship hulls is implemented, then persistent TBT in sediment will act as a secondary source of pollution to surrounding water column and biota.

In Korea, several monitoring studies on TBT contamination in sediments have been conducted since the mid 1990s [10,14,17]. However, there is a lack of information on TBT contamination in the vicinity of a large shipyard, though Korea leads the world in ship-building activity. There is no strict domestic regulation on controlling shipyard effluent containing TBT [18]. The objective of this study was to characterize butyltin contamination in sediments close to dry-docks and surface water run-off outfalls of a large scale shipyard and the surrounding bay environment, soon after the total ban of TBT use in Korea. Temporal change of TBT contamination in sediment was evaluated to validate effectiveness of the TBT regulation. Thus, age-dated sediment cores were analyzed to evaluate TBT contamination in comparison with the history of ship-building activity in the past several decades.

2. Materials and methods

2.1. Study areas and sample collection

Gohyeon Bay is located in the south coast of Korea. The average depth of the inner bay area is approximately 15 m, and the outer bay

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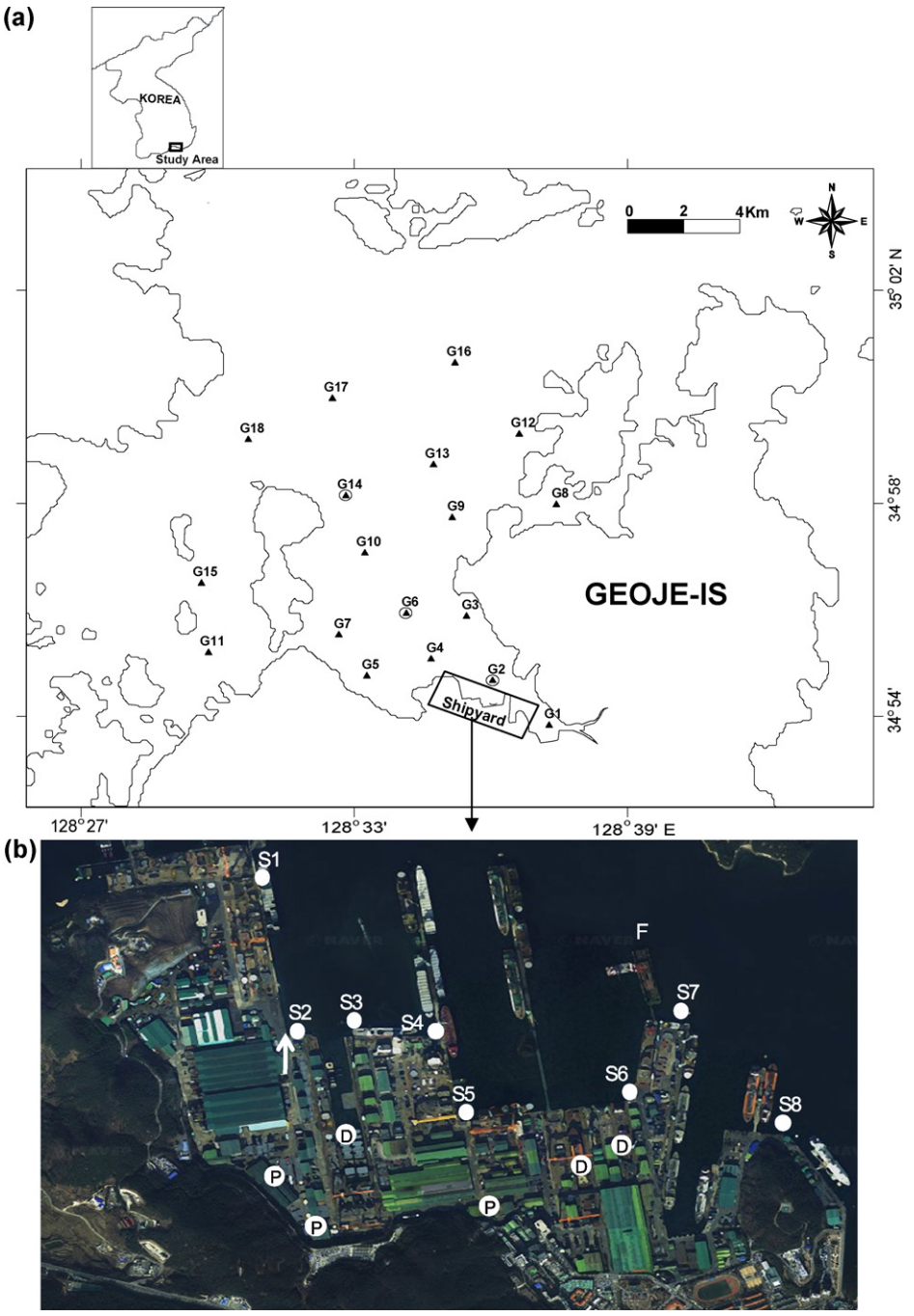

Fig. 1. Map of surface sediment sampling location (a) in Gohyeon Bay (solid triangle; G1–G18) with three sediment cores (open circle; G2, G6 and G14) and (b) near a shipyard (solid circle; S1–S8). Note: D, dry-docks; F, floating-dock; P, painting facility; an arrow indicates surface runoff outfall.

is 25 m. One of the biggest shipyards in Korea is situated along the shoreline of the inner bay. This shipyard builds various new ships since 1977. No repairing and maintenance operation of old ships has been done in the shipyard. Unlike other large shipyards in Korea which are generally located together with a big commercial harbor accommodating many ocean going vessels in a bay, the shipyard in the study area is located remotely from commercial harbors. The bay is semi-enclosed with limited water circulation. Therefore, this study area would be a good place to monitor the effectiveness of TBT regulation, as any new application of TBT based paints is prohibited and the absence of any old ships with an expiring five-year guaranteed TBT antifouling paint on ship hulls.

Eighteen surface sediment samples (G1–G18) (approximately, top 2 cm) were taken in Gohyeon Bay using a "van Veen" grab sampler in November 2003 (Fig. 1a). Additional 8 surface sediment samples (S1–S8) were collected in March 2004 close to dry-docks and surface water run-off outfalls which pass through shipyard painting facilities (Fig. 1b). Sediment core samples were taken from three stations (G2, G6, and G14) in May 2004 (Fig. 1a). Sediment core samples were taken with a SCUBA diving using an acryl barrel (12 cm i.d × 40 cm length). The sediment core from G2 was sectioned in 0.5 cm or 1 cm interval to a depth of 30 cm from core top, and the other cores from stations G6 and G14 were sectioned in 2 cm interval to a depth of 40 cm. A series of surface sediment

Table 1
Concentration and composition of butyltin compounds in surface sediments from Gohyeon Bay (G1–G18) and near a shipyard (S1–S8), South Korea (see Fig. 1 for location of stations).

Stations	Concentration (ng Sn/g dw)				%TBT[a]	BDI[b]
	MBT	DBT	TBT	$\sum$BT[c]		
Gohyeon Bay (2003)						
G1	63	32	69	164	42	1.4
G2	365	735	1624	2724	60	0.7
G3	17	26	65	108	60	0.7
G4	32	94	231	357	65	0.5
G5	59	100	149	308	48	1.1
G6	15	35	129	179	72	0.4
G7	20	45	91	156	58	0.7
G8	15	19	26	60	43	1.3
G9	17	30	59	106	55	0.8
G10	13	24	48	85	56	0.8
G11	42	64	83	189	44	1.3
G12	19	8	13	40	33	2.0
G13	17	16	33	66	50	1.0
G14	27	48	54	129	42	1.4
G15	29	26	37	92	40	1.5
G16	13	11	15	39	38	1.6
G17	13	14	16	43	37	1.7
G18	18	9	21	48	43	1.3
Shipyard (2004)						
S1	62	116	458	635	72	0.4
S2	3240	12,003	36,292	51,535	70	0.4
S3	470	1520	4973	6963	71	0.4
S4	900	2437	6726	10,063	67	0.5
S5	565	1353	3647	5565	66	0.5
S6	484	750	1961	3195	61	0.6
S7	430	809	1938	3177	61	0.6
S8	134	139	361	634	57	0.8

[a] $[TBT]/[\sum BT] \times 100$.
[b] Butyltin degradation index: ([MBT] + [DBT])/[TBT].
[c] Sum of mono-, di- and tributyltin.

sampling campaigns has been done to evaluate temporal change of butyltin levels at six stations of G2, G6, G10, G13, G16 and G18 in August 2007 and 2008 and March 2010, respectively (Fig. 1a). All sediments were frozen immediately after collection and stored at −20 °C before analysis.

2.2. Analysis of butyltins in sediment

The sediment samples were analyzed based on the method of Shim et al. [10], with some modification. For butyltin analysis, freeze-dried surface sediments were ground. The powdered samples were sieved through 200 μm mesh and weighed to about 5 g ± 0.2 g in 50 ml polypropylene centrifuge tubes. Tripentyltin chloride (Kanto, Tokyo) was added to samples as a surrogate recovery standard. The samples were digested in 10 ml of 50% HCl (Merck) and subsequently extracted with 20 ml of 0.1% of tropolone (Waco, Japan) in dichloromethane (Burdick & Jackson) for 3 h through shaking. After 10 min centrifugation (4000 rpm), a 2 ml of organic extract was transferred to a 15 ml glass test tube and concentrated under a gentle stream of nitrogen. Then the extracts were re-suspended in 2 ml of *n*-hexane and derivatized with 250 μl of propylmagnesium bromide (2 M in THF solution, Tokyo Kasei Kogyo, Japan) during a 20 min period. The remaining Grignard Reagent was neutralized with 4 ml of 0.4 N sulfuric acid (Merck). The organic phase was recovered by centrifugation and cleaned up using 2 g of activated LC-florisil (Supelco). During clean-up, the organotin compounds were eluted with *n*-hexane. The cleaned extracts were concentrated again and spiked with tetrabutyltin (Aldrich, 93%) as an internal standard, and then analyzed by gas chromatograph (Hewlett Packard 5890 SeriesII) equipped with a capillary column (DB-5, 30 m × 0.25 mm i.d. × 0.25 μm film thickness) (J&W Scientific) and a flame photometric detector. A filter with a range from 625 to 2000 nm (Dietrich Optical) was mounted on the flame photometric detector. Under splitless injection mode, 2 μl of sample was injected. The gas chromatograph operating condition was reported elsewhere [10,18].

The method detection limits of monobutyltin (MBT), dibutyltin (DBT), and TBT in sediment samples were 5.8, 3.9 and 3.3 ng Sn/g dry weight, respectively. Recoveries of three butyltins from spiked sediment samples (20 ng/g, $n = 5$) ranged from 73 to 128%. All butyltin concentrations reported in this study are expressed as tin on a dry weight basis (ng Sn/g dw).

2.3. Sediment core age dating

The excess of ^{210}Pb (half-life of 22.3 year) was measured following the method of Hong et al. [19]. One gram of the freeze-dried sediment sample was put into a Teflon beaker and then 1 ml of ^{209}Po (7.04 dpm) and 10 ml of Aqua regia ($HCl:HNO_3 = 3:1$) was added to the samples. The beaker was heated for 12 h at 80–90 °C to dry, to which 30 ml of 2 M HCl was added. The sediment was allowed to stand for 2 h at room temperature and then centrifuged for 10 min. The supernatant was transferred to a beaker containing 100 ml of polymethylpentene. After adding 3 g of ascorbic acid to the beaker, it was shaken until the sample turned colorless. Pre-cleaned silver plate was mounted on Perspex disc holder and submerged in the solution in a beaker for plating up to 12 h. After plating, the silver plate was washed with distilled water and decay was measured with alpha detector for 24 h. ^{210}Pb derived sedimentation rate was calculated based on a one-dimensional, steady-state constant ^{210}Pb flux/constant sedimentation model. The sediment depth in core

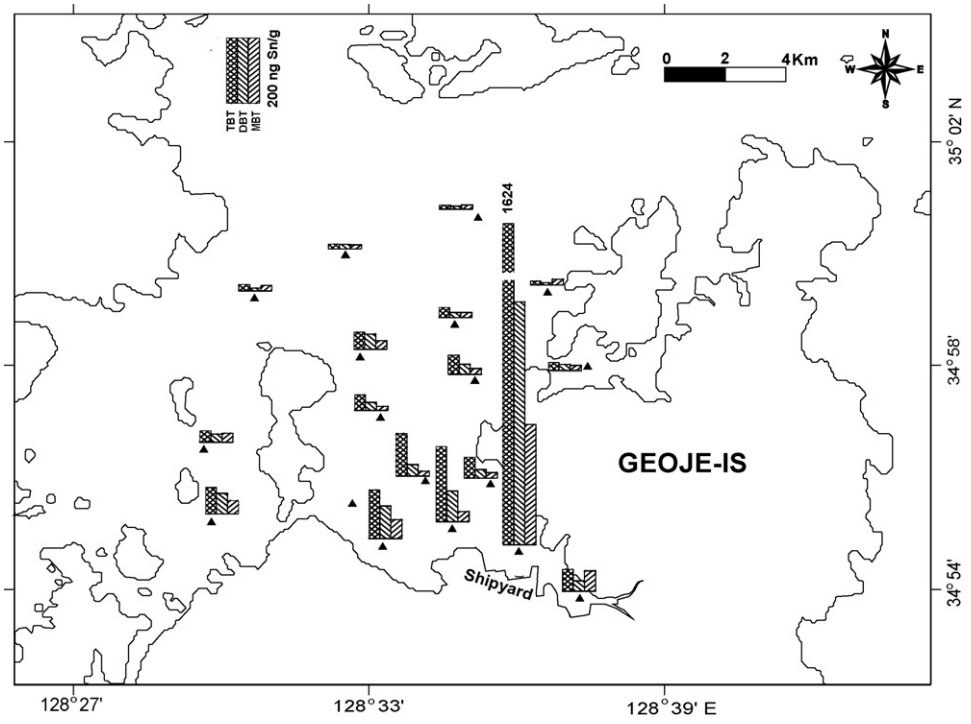

Fig. 2. Spatial distribution of concentrations of three butyltin compounds in surface sediment from Gohyeon Bay in 2003.

samples can be converted to its corresponding age by dividing the calculated sedimentation rate.

3. Results and discussion

3.1. Horizontal distribution of butyltins in 2003 and 2004

The spatial distribution of butyltin contamination in surface sediments at eighteen stations (G1–G18) in Gohyeon Bay in 2003 is presented in Table 1 and Fig. 2. TBT and $\sum$BT [sum of MBT, DBT, and TBT] concentrations in sediments from Gohyeon bay ranged from 13 to 1624 ng Sn/g and 40 to 2724 ng Sn/g, respectively. The highest concentration of TBT and $\sum$BT was found at station G2 which was the nearest to the shipyard among eighteen stations surveyed. The average TBT concentration (±standard deviation) at stations relatively close to the shipyard (G1–G7) was 347 ± 566 ng Sn/g, while the average TBT concentration was 37 ± 22 ng Sn/g at the other stations in the outer bay area (G8–G18). TBT and $\sum$BT concentrations in close to the shipyard stations (G1–G7) were significantly (Mann–Whitney Rank Sum test; $p = 0.001$ for TBT and $p = 0.003$ for $\sum$BT) higher than those in the outer bay area (G8–G18). Distribution of TBT to $\sum$BT concentrations (ng Sn/g) in sediments through transect line from G2 to G17 including G4, G6, G10, and G14 showed an apparent exponential decrease with the distance (km) from G2 ($y = -176 \ln(x) + 396.37$; $r^2 = 0.99$; $p < 0.001$) (Fig. 2).

The butyltin contamination of surface sediments in front of dry-docks and a floating-dock was additionally investigated at eight stations (S1–S8) (Fig. 1b and Table 1). TBT, DBT and MBT concentrations in surface sediment from the shipyard varied from 361 to 36,292 ng Sn/g, 116 to 12,003 ng Sn/g, and 62 to 3240 ng Sn/g, respectively. These butyltin levels are over one order of magnitude higher than those found in Gohyeon Bay. Exceptionally high TBT (36,292 ng Sn/g) and $\sum$BT (51,535 ng Sn/g) were detected at S2 where not only the largest dry-dock and the largest painting facility of the shipyard, but also a surface runoff outfall was located near the dry-dock (Fig. 1b). TBT concentrations in sediments ranged from 1938 to 6726 ng Sn/g at five stations (S3–S7) in the middle of the shipyard, while the other two stations which were about 1 km off from a dry-dock at both the West and the East ends of the shipyard (Fig. 1b) showed relatively low TBT concentrations of 361 ng Sn/g at S1 and 458 ng Sn/g at S8.

High TBT concentration at ppm level in surface sediments from the shipyard region and a TBT concentration gradient from the shipyard towards the outer Gohyeon Bay indicates that the shipyard is a major TBT input source in the bay. Average compositions of TBT (66%), DBT (23%) and MBT (11%) to $\sum$BT in sediment from stations S1–S8 close to the shipyard demonstrated higher TBT portion compared to those of TBT (49%), DBT (27%) and MBT (23%) from stations G1–G18 in Gohyeon Bay. In addition, average Butyltin Degradation Index (BDI = [MBT + DBT]/[TBT]) at S1–S8 was 0.53, while BDI was 1.12 at G1–G18. BDI value of less than 1 implies fresh input of TBT [3,20]. Relatively high TBT portion in $\sum$BT at stations near the shipyard also indicates that they have received recent TBT input from the shipyard.

The shipyard has stopped to use TBT based antifouling paints since 2002, one year ahead of a total ban in 2003. Inspection of antifouling paints applied to 17 ship hulls in the shipyard in February 2005 confirmed that all the new ships under construction at that time were painted with TBT-free antifouling paints (data not shown). However, discharging water collected from a surface runoff outfall (Fig. 1b) near the largest dry-dock and painting facility from November 2003 to August 2004 for four seasons showed TBT concentrations in the range of 1106–2392 ng Sn/L (unpublished data). Although TBT based antifouling paints were no longer used in the shipyard since 2002, surface water passing through the shipyard still contained TBT and eventually contaminated the surrounding environment. In our previous study, mussel transplanted in the same shipyard area accumulated waterborne TBT at high levels [18]. Other studies point out that not only direct TBT input from the ship hulls, but also wastewater effluent from a shipyard may contaminate receiving water and sediment around a shipyard [7,15].

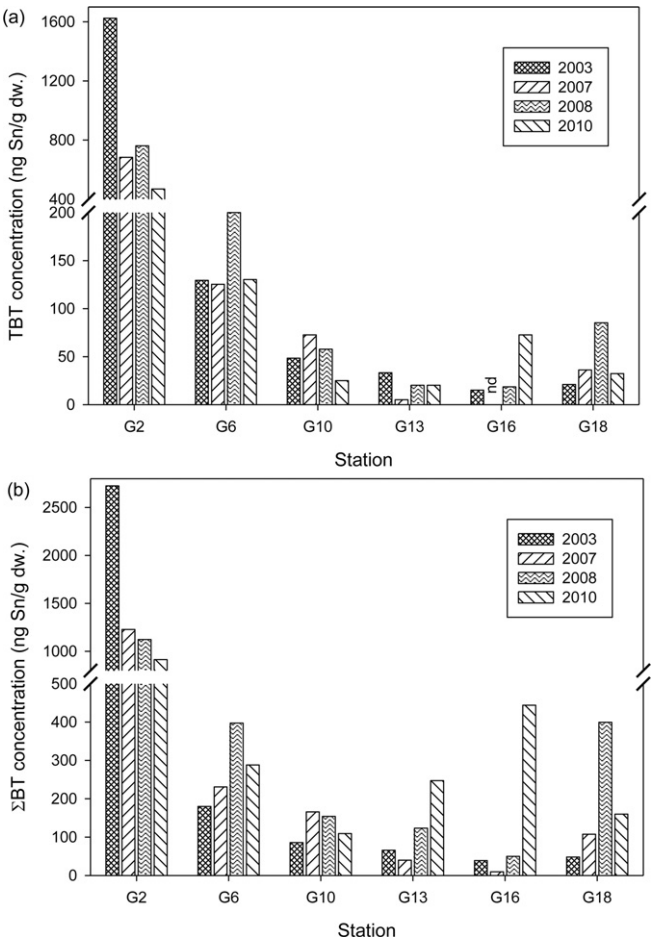

Fig. 3. Temporal change of concentrations of (a) TBT and (b) $\sum$BT at six stations in Gohyeon Bay in 2003, 2007, 2008 and 2010.

3.2. Temporal change of butyltin concentrations in 2007–2010

Additional monitoring studies were conducted in Gohyeon Bay to evaluate contamination of persistent organic pollutants including butyltins in 2007, 2008 and 2010. These motoring studies shared six stations (G2, G6, G10, G13, G16, and G18) with the butyltin monitoring survey in 2003. Thus, temporal change of TBT and $\sum$BT concentrations at six stations before (2003) and after (2007, 2008 and 2010) the total ban on use of TBT in Korea was evaluated (Fig. 3). TBT concentrations in sediments at six stations ranged from nd to 684 ng Sn/g (mean ± standard deviation; 154 ± 264 ng Sn/g) in 2007, from 18 to 762 ng Sn/g (191 ± 288 ng Sn/g) in 2008 and from 20 to 469 ng Sn/g (125 ± 174 ng Sn/g) in 2010, respectively. The maximum concentrations were detected at G2 among six stations in all the sampling campaigns from 2003 to 2010. TBT and $\sum$BT concentrations at G2 close to the shipyard showed steep reduction in levels between 2003 and 2007 four years post – TBT ban in Korea, and then followed by slight decreasing trend from 2007 to 2010. On the other hand, TBT and $\sum$BT concentrations at the rest of five stations did not show any decreasing trend. Temporal variation of TBT concentrations in 2003 was compared with those in 2007, 2008 and 2010, respectively, using Mann–Whitney Rank Sum test. TBT concentrations in 2003 were not significantly different with those in 2007 ($p = 0.82$), 2008 ($p = 0.59$) and 2010 ($p = 0.94$), respectively. The mean percent composition of TBT to $\sum$BT concentration at six stations decreased from 53% in 2003 to 27% in 2010. Nationwide TBT monitoring study in coastal environments of Korea during 2001–2005, right after the ban of TBT based paint on small ships in 2000, showed dramatic reduction in levels in seawater and to a lesser extent in bivalves, but not significantly in sediments [27]. In fact, Diez et al. [3] reported that there was no significant reduction of TBT concentrations in sediment from commercial harbors of the Catalan Sea following 10 years of TBT regulation in Spain.

3.3. Comparison of butyltin contamination with other studies

TBT levels in sediment usually show a steep concentration gradient from a source such as marina or shipyard [10,14]. On the other hand, fluctuation in TBT concentration from a given source is noted in this study (Fig. 1b and Table 1). This may reflect the fact that TBT load may arise from various nearby sources; moreover, water exchange rate and sedimentation process in the study area, and particle size and organic carbon contents in sediment may also influence the accumulation in sediment. Thus, direct comparison of mean or median concentrations among different geographic regions with different input sources will not necessarily be meaningful. However, an attempt has been made here to compare TBT levels in this study to those in literature in which a study area was described including a shipyard and (or) a dockyard (Table 2). Concentration of three butyltin compounds were compared to get better understanding of TBT contamination related to shipbuilding activity.

The highest TBT concentration (36,292 ng Sn/g) in this study near a dry-dock is lower than 141,000 ng Sn/g reported near a dock in Antwerp Harbor, Belgium [7], but comparable to 39,300 ng Sn/g in Venice lagoon, Italy [21]. Sediment TBT concentrations near a shipyard in Otuschi Bay (14,000 ng Sn/g) in Japan and Chennai port (11,871 ng Sn/g) in India were a little lower than our values in this study but in the same order of magnitude [9,12]. Except for some studies reporting tens (or hundreds) of ppb of TBT levels (Sado Estuary, Kaohsiung Harbor, and Gohyeon Bay) [22–24], the other regions in Table 2 showed TBT concentrations in the range of from 1137 to 5372 ng Sn/L [8,24–26]. TBT concentrations in surface sediments from Gohyeon Bay in this study are higher than levels reported in other shipyard areas in Ulsan Bay (13,300 ng Sn/g) and Okpo Bay (11,700 ng Sn/g), South Korea in 1996, 7 years before the total ban of TBT [14].

3.4. Vertical distribution of butyltins

When time series monitoring data or archived historical samples are absent in an area, an undisturbed, age-dated sediment core can provide valuable information on pollution history. Time resolution in a sediment core depends on the sedimentation rate of a particular area. Three sediment core samples were taken with reference to distance from a shipyard in order to understand the past TBT contamination history in this bay. Vertical profiles of three butyltin concentrations in sediment cores from stations G2, G6, and G14 were shown in Fig. 4 with an inferred sediment chronology based on ^{210}Pb dating [14]. The ^{210}Pb profiles in three cores did not show any major disturbance and demonstrated a significant correlation with core depth from the surface. Sedimentation rates of cores at G2, G6 and G14 were estimated with ^{210}Pb excess data as 0.57, 0.44 and 0.51 cm/year, respectively, which cover TBT contamination history back to the early 1920s.

The TBT concentration in core sediments varied depending on the stations, from 6 to 2961 ng Sn/g for G2, nd to 450 ng Sn/g for G6 and nd to 130 ng Sn/g for G14 (Fig. 4). The maximum TBT levels were detected in the core-top sediments, and they were about 2 times higher than those of surface sediment samples at the same stations. Although the surface sediments and sediment cores were taken at same stations, it was hard to take samples from the exact same position. In addition, samples were collected in different time

Table 2
Maximum concentrations of butyltin compounds in sediments from different shipyard (or dock) areas in the world.

Study area (sampling year)	Concentrations (ng Sn/g dw)			Reference
	MBT	DBT	TBT	
Sado Estuary, Portugal (2007)	443	56	66	[22]
Kaohsiung Harbor, Taiwan (2006)	7	18	125	[23]
Gohyeon Bay, South Korea (2002–2004)	–[a]	126	569	[24]
Santa Catarina Harbor, Brazil (2008)	95	36	1137	[8]
Busan Harbor, South Korea (2002–2004)	–	1080	2698	[24]
Pasaia of port, Spain (2007)	125	2874	3132	[25]
Puerto Belgrano, Argentina (2005)	–	1645	3288	[26]
Busan Harbor, South Korea (2002–2004)	–	2005	4102	[24]
Ulsan Bay, South Korea (2002–2004)	–	2367	5372	[24]
Chennai port, India (2008)	1479	1512	11,871	[9]
Otsuchi Bay, Japan (2005)	3300	3400	14,000	[12]
Venice Lagoon, Italy (2003)	–	12,623	39,300	[21]
Antwerp Harbor, Belgium (1991)	46,000	103,000	141,000	[7]
Gohyeon Bay, South Korea (2003)	365	735	1624	This study
Gohyeon Bay (shipyard area) (2004)	3240	12,003	36,292	This study
Gohyeon Bay, South Korea (2007–2010)	148	213	762	This study

[a] Not available.

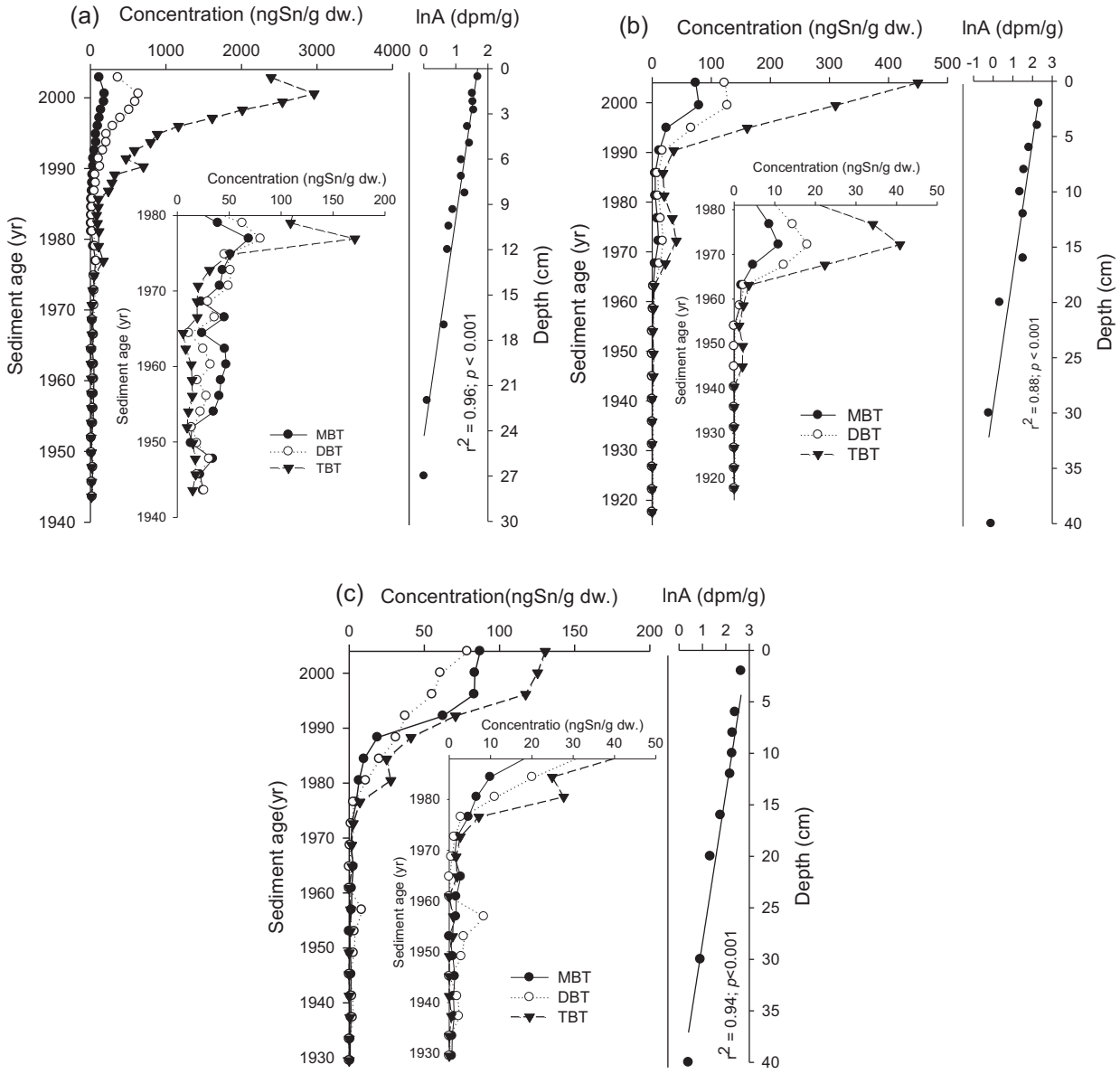

Fig. 4. Vertical profiles of butyltin concentrations and ^{210}Pb excess data in sediment cores with sediment depth from the core surface or corresponding dated sediment age at (a) G2, (b) G6, and (c) G14 in Gohyeon Bay. Note: Insertion of a graph is to enlarge concentration of butyltin below 10 cm depth.

(November, 2003 and May, 2004), which may reflect change of concentrations. The other possibility is different sampling methods (grab *vs* hand corer; see Section 2).

Even though TBT was detected at all depths in sediment core from G2, TBT concentration was less than 20 ng Sn/g below 20 cm depth from the core surface. TBT was below detection limit from 16 cm depth at G6 and from 12 cm at G14. DBT and MBT concentrations in three core sediments ranged from nd to 638 ng Sn/g and nd to 189 ng Sn/g, respectively. Overall TBT concentrations in the three core samples were relatively lower than those in the core samples at Okpo and Ulsan bays (>8000 and >40,000 ng Sn/g), Korea [14]. Among three butyltins, TBT was dominant (44% of $\sum$BT) in all three core samples followed by DBT and MBT at G2 and G6. MBT concentration was a little higher than that of DBT at G14. The ratio of [TBT]/[DBT] ($R_{[TBT]/[DBT]}$) in environmental sample can be used as an indicator of old or new ($R_{[TBT]/[DBT]} > 5$) contamination [28]. The $R_{[TBT]/[DBT]}$ profile of core sediment at G6 and G14 gathered around 2 except for a few points, but $R_{[TBT]/[DBT]}$ at G2 were less than 2 below 12 cm and in between 3.5 and 6.5 above 12 cm to core top sediment (Fig. 5). These results indicate that TBT contamination in

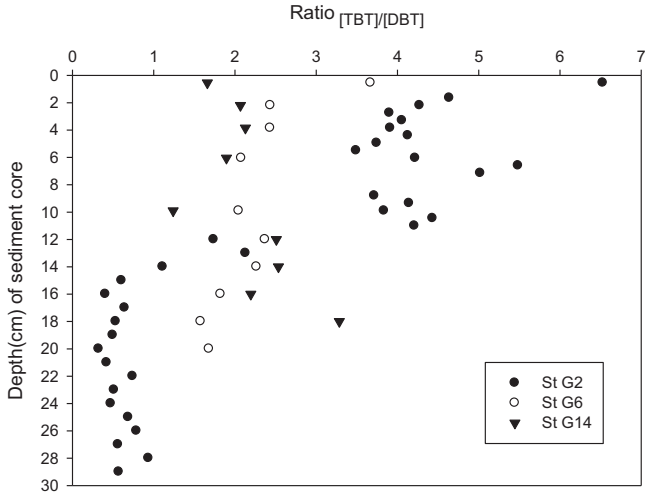

Fig. 5. Ratio of [TBT]/[DBT] ($R_{[TBT]/[DBT]}$) with corresponding core depth from the core surface at G2, G6, and G14.

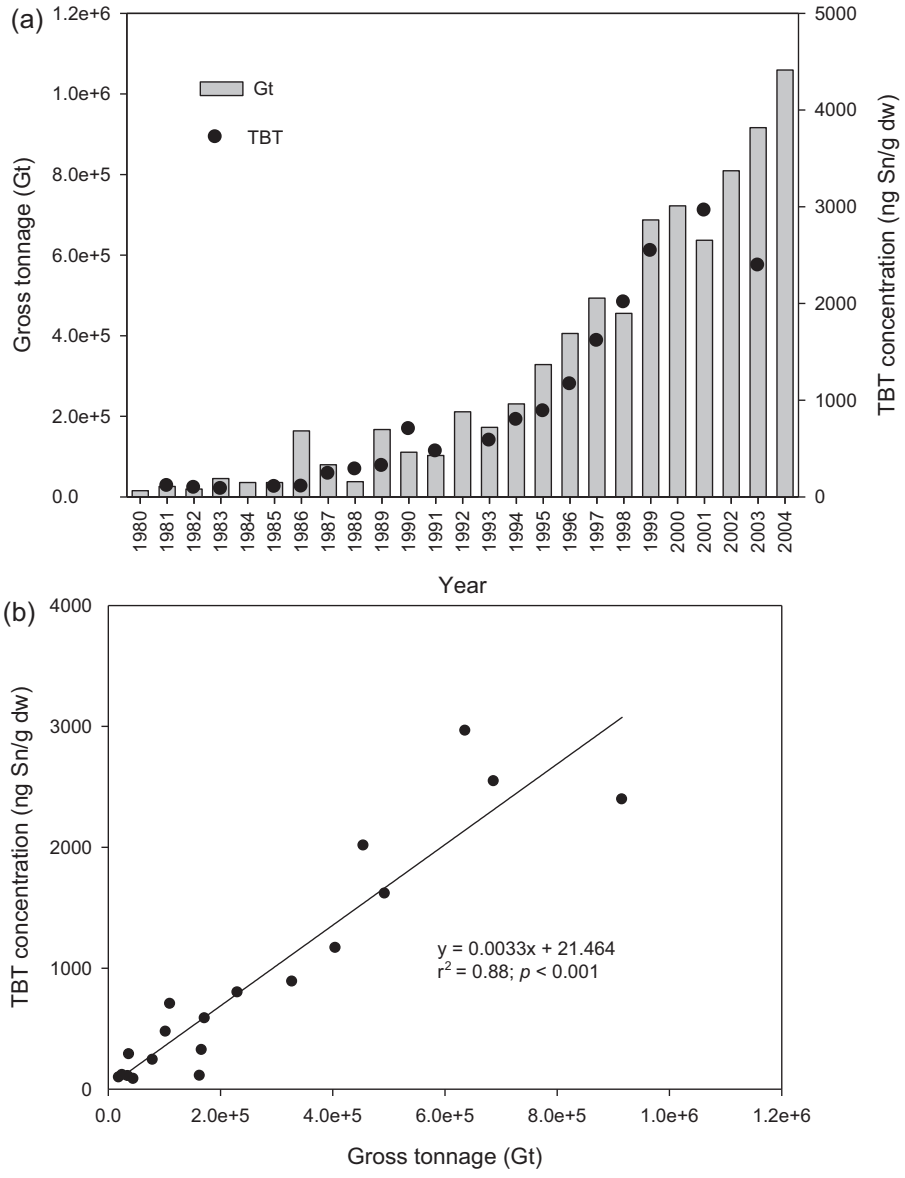

Fig. 6. (a) Annual production of ships in gross tonnage and TBT concentration in sediment core with the ^{210}Pb dated-age at station G2 and (b) their linear regression.

core sediment at G6 and G14 are relatively older (or further from a source) than that at G2. Further the distance from a source means, the longer time it takes to travel and more the possibility of photolysis and microbial degradation from TBT to DBT in water column. In addition, TBT can be adsorbed to suspended particle in water column due to higher Log K_{ow} value (2.6) than DBT (1.49) and MBT (0.35) [29] and settle down in benthic environments closer to the source area than DBT and MBT. Significant correlations between log transformed TBT and DBT ($r^2 = 0.89$; $p < 0.001$) as well as TBT and MBT ($r^2 = 0.78$; $p < 0.001$) indicates that DBT and MBT found in core sediments are mainly degradation products of TBT.

The vertical profiles of TBT concentrations in three core sediments revealed that TBT contamination increased rapidly from the early 1980s in the study area. The first ship was launched in 1980 from the shipyard and the gross tonnage of ships built in the shipyard increased subsequently in the following two decades (Fig. 6a). Exponential increase of shipbuilding in 1990s corresponds well with exponential increase of TBT concentration in G2 core sediment. Increase of TBT concentrations in core sediment at G2 showed a significant positive correlation ($r^2 = 0.88$, $p < 0.001$) with the corresponding gross tons of ships built in the shipyard (Fig. 6b). Even though TBT could have been degraded to DBT and MBT, its vertical profile was well preserved in the undisturbed sediment core samples in this study.

In our previous study, sediment cores from two different shipyard areas in Ulsan and Okpo Bays in Korea in 1996 showed an obvious high TBT profile [14]. Though this study was conducted in another part of Korea, similar high TBT profile was found until 2004. The shipyard at Gohyeon Bay has built hundreds and thousands tons of ocean going vessels. Korean government has banned TBT usage in antifouling paints on ocean going vessels (>400 tons) since November 2003. Antifouling paint application statistics in the shipyard in Gohyeon Bay showed that TBT usage existed until 2001. Current study supports this observation. South Korea is leading the world in shipbuilding industry [30]. Highly accumulative TBT in sediment needs to be monitored in shipyard areas in Korea, even after the total ban of TBT in Korea. Historical data on TBT contamination derived from sediment core samples in this study will be useful in monitoring the overall effectiveness of TBT regulation, especially near a shipyard. In addition, IMO AFS Treaty requires complete removal of TBT based paint from ship hulls till 2013, five years after a ban on new application. There is growing concern for treating removed TBT paint chips and TBT contaminated effluents from a dry-dock.

3.5. Ecotoxicological concern

Sediment bound TBT is known to cause adverse biological effects on benthic organisms [31–33]. Concentrations of TBT determined in surface and core sediments in this study were compared with sediment quality guideline values proposed mainly to protect marine benthic life (Fig. 7). When the lowest, Australian Sediment Quality Guideline-low trigger value of 5 ng Sn/g [34] was applied, all the values in surface sediment samples and about 50–70% of core sediment samples analyzed in this study exceeded this limit. Approximately 50% of both the surface and the G2 core sediments were over the Australian Sediment Quality Guideline-high trigger value of 70 ng Sn/g [34], while only TBT values in top ~5 cm of core sediment exceeded in G6 and G14 cores. Chronic toxic effects on amphipods and polychaetes were expected in about 60% of surface and G2 core sediment samples and about 20% of G6 and G14 core sediment samples based on the value of 41.2 ng Sn/g *in vivo* sediment toxicity test [31]. Forty percent of each surface (S1–S8) and G2 core (>1990 year) sediment samples exceeded the value of 300 ng Sn/g which has caused chronic effects on benthic clam [32,33]. Even though TBT was totally banned in Korea since

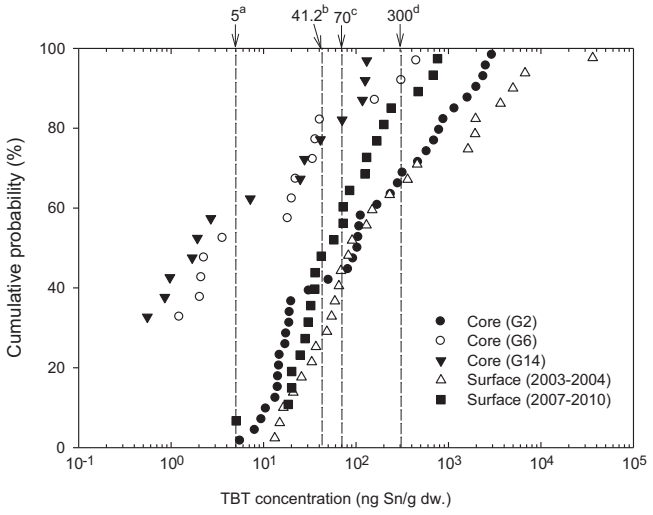

Fig. 7. Cumulative probability of TBT concentrations in surface sediment samples (G1–G18 and S1–S8) from Gohyeon Bay including a large scale shipyard and three sediment core samples (G2, G6 and G14) with comparison of TBT sediment quality guideline or screening values reported elsewhere. (a) Australian sediment quality guideline-low trigger value [34], (b) Chronic effects on amphipods and polychaetes [31] (converted to ng Sn/g), (c) Australian sediment quality guideline-high trigger value [34], and (d) Chronic effects on clam [32,33].

November, 2003, residual concentrations of TBT in surface and core sediments around a large scale shipyard well exceeded sediment quality guideline values. Organic pollutants degrade slowly in benthic environments [17,35] and high levels of toxic TBT interfere with microbial degradation [3]; hence it may take a long-time to reduce sediment TBT levels well below the quality guideline values.

4. Conclusion

Exceptionally high concentrations of TBT were determined in surface sediments close to a dry-dock and a surface runoff outfall in a large scale shipyard. Two decades of TBT contamination, especially an exponential increase in 1990s, was revealed with age-dated sediment core. A large shipyard has acted as a major TBT input source in the study area before TBT total ban and to a lesser extent after the ban. Even though TBT was no longer used in Korea since 2003, sediment TBT levels did not significantly decrease following the 7 years after TBT total ban and exceeded the sediment quality guideline or screening values reported or applied in the world. It is extremely important to monitor sediment TBT contamination near shipyard areas until the levels fall well below the guideline or screening values.

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