Analysis of antifouling agents after regulation of tributyltin compounds in Korea

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ABSTRACT

Diverse new antifouling agents are being used as replacements for the organotin compounds that are currently being banned. A comprehensive study on Korea's major seaports was conducted between 2006 and 2009 to assess the concentrations of butyltin compounds and new antifouling agents (chlorothalonil, dichlofluanid, Irgarol 1051). The constituents of the pollution due to antifouling agents in major seaports on the Korean peninsula are shifting from butyltin compounds to new antifouling agents. Also, the distribution of traditional butyltin compounds has centered on the east and west coasts, and the new antifouling agents have polluted the south and east coasts. With the results of this study, our lab was able to identify key locations within Korea where focused pollution control of antifouling agents is necessary.

1. Introduction

Over the past several decades, the use of tributyltin (TBT) compounds on the coast of Korea has had negative effects on the marine ecosystem, such as imposex. In response, the Korean government and International Maritime Organization (IMO) banned the use of TBT in 2003. As a result, the consumption of new, alternative antifouling agents was expected to increase [1].

After the ban of TBT, the antifouling industry tried to find an alternative; consequently, numerous chemicals have been introduced and embraced by the industry. Although these chemicals were produced to replace toxic TBT, it has been difficult to eliminate toxins from them. Therefore, many nations are identifying the toxins and the extent to which they pollute [2–4].

Among them, Irgarol 1051 has been reported to disturb the electron transfer process within Photosystem-II and have fatal effects on marine life [5]. The inhibition of photosynthesis due to Irgarol 1051 occurs at concentrations as low as $1.0\,\mu g/L$ [6]; in addition, Irgarol 1051 has a relatively long half-life (200 days). Thus, it requires continuous observation. Several countries have already banned its use.

Chlorothalonil and dichlofluanid have very short half-lives of 4 weeks [3] and 0.8 days [7], respectively. As a result, many ships use these chemicals as antifouling agents. However, it is impossible for these chemicals to lack toxicity—when excessive amounts of

these materials are injected into rats, the rate of cancerous tumor development increases, as does chronic renal failure [8]. Dichlofluanid has a lower toxicity compared with other antifouling agents, although some studies have identified it as having toxic effects. Many studies have already been conducted on these substances as herbicides with regard to the levels of toxicity and their distribution substances in soil and streams [9–11].

It was expected that the concentrations of these new antifouling agents would increase after the ban of TBT and the corresponding reduction in butyltin compound concentrations in the marine ecosystem. However, in a few recent reports, high concentrations of butyltin compounds and new antifouling agents are being noted in the same areas [12,13]. It is entirely possible that this finding could be due to remnants of past butyltin compound use, but because high concentrations of TBT are being identified in many areas, it is safe to assume that TBT is still being used as an antifouling agent. If this is indeed the case, unlike the past—in which only butyltin compounds were used—it is believed that this situation will create a new complex marine ecosystem and environment of contamination. Many researchers have reported that when butyltin compounds and new antifouling agents persist together, a higher level of toxicity results. It was reported that in the mixture toxicity test of TBT, Irgarol 1051, and Sea-nine, the toxicity to *Scenedesmus vacuolatus* was slightly overestimated compared with that of the individual compound, and the mixture of Irgarol 1051 and chlorothalonil also had a toxicity to *Dunaliella tertiolecta*, which was 1.5 times higher [14,15]. Thus, it has been concluded that the study of coastal environments and antifouling agents requires the simultaneous investigation of butyltin compounds and new antifouling agents.

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Table 1
Location of sampling points.

		Latitude °N	Longitude °E	Classification
Ganghwa	G1	37°38′21.46″	126°23′06.56″	A
	G2	37°40′48.12″	126°23′55.33″	A
	G3	37°42′00.51″	126°22′52.26″	A
Inchon	I1	37°27′12.03″	126°36′41.45″	B
	I2	37°27′28.28″	126°36′04.15″	B
	I3	37°30′11.09″	126°38′22.78″	B
Asan	A1	36°59′03.55″	126°49′23.02″	F
	A2	36°58′15.43″	126°49′57.59″	F
	A3	36°57′26.90″	126°50′36.49″	B
	A4	36°56′50.99″	126°48′17.83″	F
	A5	36°58′58.28″	126°45′38.95″	A
	A6	36°53′24.63″	126°49′35.12″	F
Gunsan	Gu1	36°58′15.94″	126°37′06.73″	B
	Gu2	35°58′40.99″	126°37′30.95″	B
	Gu3	35°58′58.51″	126°40′35.26″	F
	Gu4	35°59′30.33″	126°42′46.27″	F
Yosu	Y1	34°45′09.50″	127°45′10.35″	F
	Y2	34°44′48.43″	127°44′57.63″	F
	Y3	34°44′33.90″	127°45′25.36″	MC
	Y4	34°43′46.63″	127°43′37.15″	F
Masan	M1	35°10′30.39″	128°34′16.74″	B
	M2	35°11′35.39″	128°34′16.74″	B
	M3	35°12′37.91″	128°35′38.21″	B
	M4	35°12′10.05″	128°35′38.42″	B
	M5	35°10′47.21″	128°35′33.79″	B
Busan	B1	35°04′02.31″	128°59′44.71″	B
	B2	35°04′57.75″	128°59′50.91″	B
	B3	35°04′19.94″	129°00′19.47″	B
	B4	35°04′52.80″	129°01′34.12″	B
	B5	35°05′38.06″	129°02′09.60″	B
Ulsan	U1	35°31′40.80″	129°22′34.28″	B
	U2	35°31′20.28″	129°22′33.70″	B
	U3	35°30′12.06″	129°23′15.66″	B
	U4	35°30′10.13″	129°22′44.35″	MC
	U5	35°30′10.88″	129°22′01.91″	B
Donghae	D1	37°29′40.17″	129°08′36.00″	B
	D2	37°29′29.81″	129°08′04.72″	B
	D3	37°29′27.85″	129°07′52.40″	B
	D4	37°29′40.04″	129°07′56.61″	MC
Sokcho	S1	38°12′24.15″	128°35′54.07″	MC
	S2	38°12′21.76″	128°35′37.34″	F
	S3	38°12′32.87″	128°35′39.31″	F
	S4	38°12′38.26″	128°35′49.58″	F
	S5	38°12′30.64″	128°36′08.34″	F

F: fishery harbor; B: big harbor; A: agriculture; MC: military ship and coast guard ship.

The main purpose of this study was to measure the change in antifouling compound use on the coast of Korea before and after the ban of TBT in 2008 [16]. Also, the pattern of contamination was evaluated based on the type of ships that were docked and the surrounding environment.

2. Materials and methods

2.1. Chemicals

All HPLC-grade toluene was purchased from J.T Baker. Dibutyltindichloride (DBT, 96%) and tributyltin chloride (TBT, 96%) were purchased from Aldrich Chemical, Inc., triethyltinchloride (TET, 98%) was purchased from Merck, and monobutyltintrichloride (MBT, 95%) was purchased from Johnson Mattery Alfa Products. These standard materials were used without further purification. Methanolic stock solutions containing 1000 ppm of tin were prepared weekly in a 25 mL volumetric flask and stored in a dark room at 4 °C. Working solutions were prepared daily from these stock solutions. Sodium tetraethylborate was obtained from Aldrich. All HPLC grade methanol and hexane were obtained from Fisher.

Dichlofluanid (99%) and chlorothalonil (98%) were purchased from SUPELCO. Irgarol 1051 was obtained from Ciba-Geigy. The internal standard, 9-bromoanthracene, was purchased from Aldrich. Toluene stock solutions were prepared weekly in a 25-mL volumetric flask and stored at 4 °C. 9-Bromoanthracene was used by Okamura et al. as a stable internal standard to analyze new antifouling agents [17].

2.2. Seawater sampling

There were 44 samples, comprising 13 fishery harbors, 23 big harbors, 4 harbors adjacent to agricultural areas, and 4 harbors that docked coast guard and military vessels (Table 1). Because fishery harbors are ports where small ships (less than 25 m) are concentrated, the usage of antifouling agents by small ships was investigated. Big harbors near industrial areas were selected, because pollution of antifouling agents by large, continuously

entering and exiting ships is expected to be high. Harbors near agricultural areas were monitored, because some new antifouling agents are used as herbicides. The monitoring of antifouling compounds in ports that docked coast guard and military vessels was also necessary, because they fell under the exception clause of non-commercial ships in the IMO's TBT ban regulation.

Samples were taken from June 18 to 21, 2006 and from July 19 to 23, 2009. Two liters of seawater were drawn from a depth of 20 cm and stored in polyethylene (PE) bottles. All samples were protected by storage in a deep freezer ($-20\,^{\circ}$C).

2.3. Extraction method

For the extraction of butyltin compounds, a 250 mL sample was taken. When NaBEt$_4$ (sodium tetraethylborate) was used as an ethylation reagent, ethylation/extraction of the butyltin compounds could be performed in seawater in a single-step procedure. A 250 mL borosilicate volumetric flask was used for this operation, into which 1.0 mL hexane and 1.0 mL sodium tetraethylborate (0.2 g/10.0 mL) were added successively and agitated vigorously on a magnetic stirrer at 2000 rpm for 1 h. The agitation was stopped, and the organic phase was transferred into a vial for injection into the GC–FPD. The efficiency of the extraction was monitored using triethyltinchloride as an internal standard; 2.0 μL of each aliquot was injected into the GC–FPD.

For extraction of the new antifouling agents, a liquid–liquid extraction method was used. To extract antifouling agents from seawater, liquid–liquid extraction methods and SPE extraction methods could be used. Recently, SPE extraction has been used more often, but liquid–liquid extraction methods can be analyzed quickly without equipment. According to research by Liu et al. there is no difference between the results from recovery tests using SPE extraction and liquid–liquid extraction [18].

All samples were passed successively through a membrane filter (0.45 μm pore size, 90 mm, Advantec). One liter of seawater was transferred into a volumetric flask, along with 200 L of the 1.0 ppm internal standard (9-bromoanthracene). Toluene (1.0 mL) was then added and vigorously stirred at 2000 rpm for 1 h to extract the agents. Agitation was stopped, and the organic phase was transferred to a vial; 3.0 μL of each aliquot was injected into the GC–MS.

2.4. Measurements on instruments

For the butyltin compounds, a Hewlett Packard 5890 II gas chromatograph (GC), equipped with a split/splitless injector, fused silica capillary column (Ultra-1, 25 m, 0.32 mm, i.d., film thickness 0.52 μm), and a flame photometry detector, was used with a 610 nm cutoff interference filter at 250 °C with hydrogen and air flow rates of 21 and 28 psi/cm^2, respectively. The temperature of the injection port was set to 300 °C. Helium, at 15 psi, was used as the carrier gas in the splitless mode for 90 s. The column temperature was programmed to hold at 60 °C for 1 min and ramp to 280 °C at 10 °C/min. The retention times were 4.5 min for the internal standard, TET; 6.6 min for MBT; 8.4 min for DBT; and 10 min for TBT.

For the new antifouling agents, a Hewlett Packard 5890 II GC, equipped with an HP 5970 mass selective detector and an Ultra-2 column (crosslinked 5% phenyl-methylpolysiloxane with a 50 m length, 0.2 mm i.d., film thickness 0.11 μm), was used. After tuning the machine, the operating conditions were optimized as follows: injector temperature, 300 °C; and split time, 80 s. The oven temperature was programmed to hold at 105 °C for 1 min and ramp 25 °C/min to 180 °C. After holding for 1 min at 180 °C, the temperature was ramped 5 °C/min to 230 °C, where it was held for 20 min. The transfer line temperature was set to 280 °C. Helium was used as the carrier gas at a pressure of 22 psi.

The target and qualifier ions that were placed in the SIM descriptor were as follows: chlorothalonil, m/z 266, 229, 205, and 168; dichlofluanid, m/z 332, 224, 167, and 154; Irgarol 1051, m/z 253, 238, 182, and 111; and 9-bromoanthracene, m/z 256, 176, and 147. An electron multiplier of approximately 200 V was used as the detector. The retention times were: 10.0 min for chlorothalonil; 11.5 min for dichlofluanid; 13.0 min for Irgarol 1051; and 13.9 min for the internal standard, 9-bromoanthracene.

2.5. Recovery rates and detection limits

For analysis of the recovery, 80 ng Sn/L of the butyltin compounds was added to the standard sample and the real seawater sample using a matrix. Replicate analyses of the spiked matrices (n = 3) demonstrated adequate precision with good recovery and repeatability. The mean recoveries (RSD) were: $94.63 \pm 1.46\%$ for MBT; $94.27 \pm 2.88\%$ for DBT; and 95.77 ± 1.22 for TBT. The calibration curves were evaluated at 5, 10, 20, 50, and 100 ng Sn/L, and all showed good linearity ($R^2 > 0.999$). The limit of detection was calculated by regression analysis per the EPA. The detection limits for mono-, di-, and tributyltin were 3.36, 2.51, and 5.34 ng Sn/L, respectively.

For analysis of the recovery, 100 ng/L of the new antifouling agent was added to the standard sample and the real seawater sample using a matrix. Replicate analyses of the spiked matrices (n = 3) demonstrated adequate precision with good recovery and repeatability. The mean recoveries (RSD) were: $73.55 \pm 1.64\%$ for Irgarol 1051; $93.83 \pm 2.34\%$ for dichlofluanid; and $120.28 \pm 4.87\%$ for chlorothalonil. The standard solution (1000 ppm) was newly prepared for every experiment when a calibration curve was drawn, because the antifouling agents can degrade quickly. The calibration curves were evaluated in the range of 5, 10, 20, 50, and 100 ng/L; all showed good linearity. The limit of detection was calculated by regression analysis, as suggested by the EPA. The respective detection limits for chlorothalonil, dichlofluanid, and Irgarol 1051 were 5.52, 1.77, and 7.66 ng/L.

3. Results and discussion

3.1. Changes in $\sum$butyltin compounds and $\sum$NEW antifouling agent concentrations between 2006 and 2009 on the coast of Korea

Changes were expected in the pollution patterns in the coastal areas of Korea after the 2008 total TBT ban. Fig. 1 shows the changes in antifouling agent distribution patterns in 2006 and 2009 in quartiles, focused on changes in $\sum$NEW antifouling agent (sum of the 3 new antifouling agents) and $\sum$butyltin compounds.

First, we found that the average $\sum$BTs (44.7 ng Sn/L) was higher than the average $\sum$NEW (10.5 ng/L) in 2006. It was further noted that average value of $\sum$NEW (50.3 ng/L) was higher than that of $\sum$BTs (25.08 ng Sn/L) in 2009. Then, we identified the change in pollutant patterns from butyltin compounds to new antifouling agents: the average values of the concentrations of pollutants indicated a decrease in butyltin compounds and an increase in new antifouling agents over time.

Based on the maximum values, however, a different pattern emerged. In 2006, the maximum $\sum$BTs value was 220.11 ng Sn/L (G1, Gunsan), and in 2009, it was 217.66 ng Sn/L (U5, Ulsan). This result suggests that the TBT pollution levels remained high in specific regions, indicating that it is required to monitor butyltin compounds continuously. Also, the maximum value of $\sum$NEW for Gunsan (Gu2) in 2009 was 215.18 ng/L, similar to that of butyltin compounds. Therefore, the continuous monitoring of new antifouling agents, as well as butyltin compounds, is required in the coastal areas.
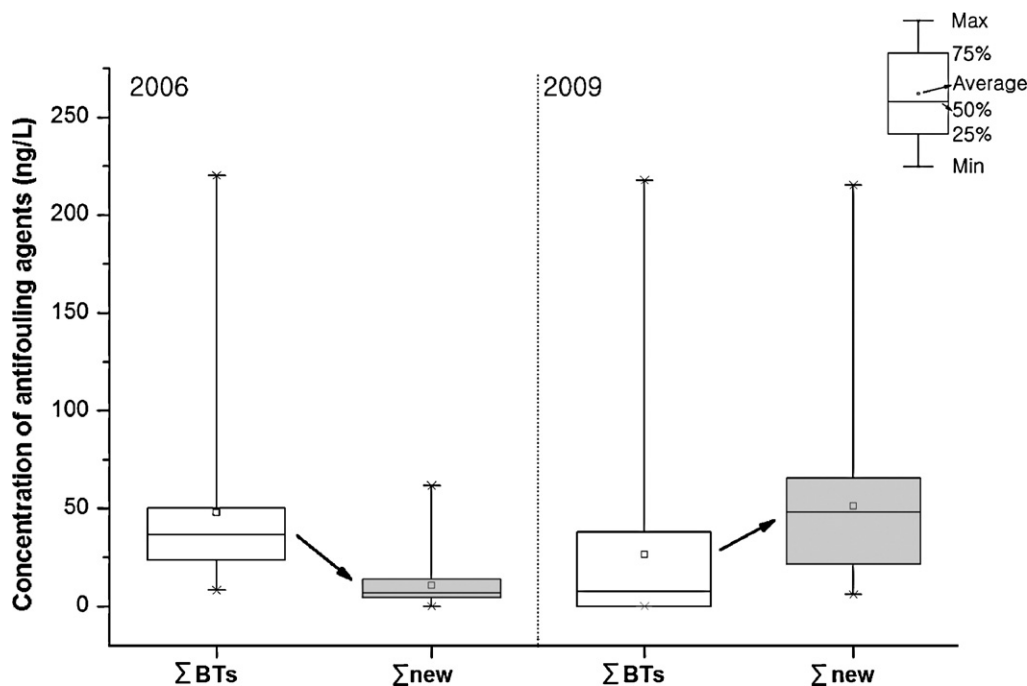
Fig. 1. Quartiles of $\sum$butyltin compound and $\sum$NEW antifouling agent concentrations in sea water between 2006 and 2009 in Korea (BT and NEW indicates butyltin compounds and new antifouling agents, respectively).

In Korea, the range of butlytin compounds was not detected (N.D.) to 217.66 ng Sn/L in 2009. Butlytin compound levels in Taiwan ranged from 9.7 to 178 ng Sn/L in 2007 and 20.6 to 83.7 ng Sn/L in India in 2008 [19]. Based on results from Korea and other countries, high concentrations of butlytin compounds still exist around the world after the TBT ban.

Yet, new antifouling agent levels in Korea ranged between N.D and 215.18 ng/L in 2009. Because dichlofluanid, a new antifouling agent, is easy to biodegrade, it was observed below the detection limit in most regions; however, there were high levels in several regions. Several countries have been in similar situations. In the UK, the dichlofluanid in black water was below the detection limit, but levels in commercial estuaries were high [20]. A maximum of 600 ng/L was detected in the seawater near Spain [21]. Concentrations of chlorothalonil ranging from N.D. to 1.38 ng/L were detected in the UK, and Irgarol 501 levels have been N.D. to 1200 ng/L in Greece [22]. Based on the literature, new antifouling agents have also been detected all over the world, necessitating its continual monitoring in Korea.

3.2. Antifouling agent levels by harbor type in 2006 and 2009

Generally, the pollution levels of antifouling agents in marine ecosystems have changed not only based on the size and number of docked ships but also the surrounding environment. We separated these patterns into 4 groups according to the type of ship and the surrounding environment (Fig. 2).

For fishery harbors, the TBT and $\sum$BTs concentrations have declined from 2006 to 2009. However, new antifouling agents, such as chlorothalonil, dichlofluanid, and Irgarol 1051, have increased in 2009. In particular, chlorothalonil and Irgarol 1051 have increased significantly compared with 2006. The high concentrations of dichlofluanid and chlorothalonil in fishery harbors have been caused by the many ships that use these agents.

For big harbors, TBT and $\sum$BTs levels had a similar trend as those in fishery harbors in 2009, but TBT was still observed in some harbors. New antifouling agents also increased overall in 2009, similar to the fishery harbors. Dichlofluanid did not change much between

2006 and 2009, while chlorothalonil and Irgarol 1051 underwent remarkable increases in concentration, suggesting that similar to fishery harbors, many ships at big harbors use new antifouling agents instead of TBT and $\sum$BTs.

For harbors near agricultural areas, the concentration of butyltin compounds decreased in 2009, but new antifouling agents were observed at relatively high levels. New antifouling agent levels in the harbors adjacent to agricultural areas were higher than those in other harbors, due to several possible reasons. Among the 3 new antifouling agents, the levels of dichlofluanid were the highest. They originated from herbicides, because new antifouling agents have been used as herbicides [4,9]. Voulvoulis et al. [20] reported that major sources of harbor pollution include not only antifouling agents used by ships but also pesticides from the agricultural sector. Because the concentrations of these chemicals in the same area were not measured as high in 2006, however, there is no other reasonable explanation.

In harbors where military and coast guard ships are docked, compared with 2006, the concentrations of TBT and $\sum$BTs were significantly higher in 2009. This result can be attributed to the increased use of butyltin compounds in these harbors due to the exclusion clause in the ban of TBT by the IMO on noncommercial ships. Because there were no regulations for these ships, we assumed that new antifouling agent levels in these harbors would be lower than in other harbors. On the contrary, the pollution levels were similar or exceeded those in other harbors. Although it is difficult to conduct a thorough investigation into the total use of antifouling agents within military facilities, the overall pollution levels in these areas should be measured to determine how the combined pollution of butyltin compounds and new antifouling agents affect ecosystems.

3.3. Distribution of concentrations by location in 2009

The regional distributions of butyltin compounds and the 3 new antifouling agents are shown in Fig. 3. The areas were largely separated into west, south, and east seas, and the pollution levels were
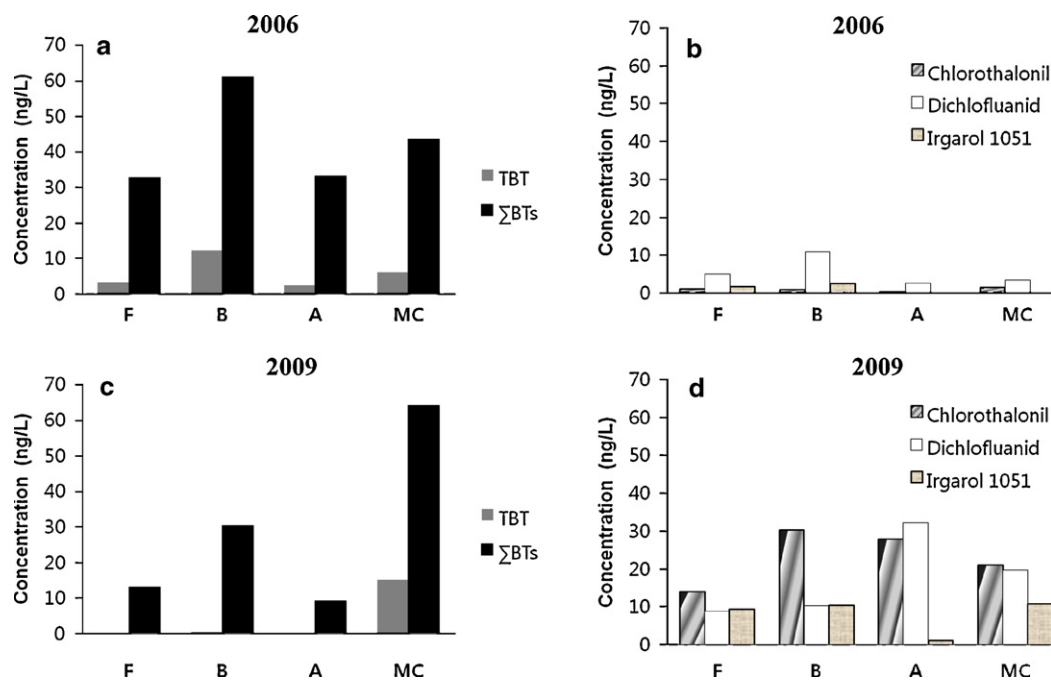
Fig. 2. Distribution of butyltin compounds and new antifouling agents according to area type: F (fishery harbor); B (big harbor); A (agriculture); MC (military and coast guard ships).

evaluated using average concentrations of the antifouling agents and frequency of detection (see Table 2).

As shown in Fig. 3, for harbors in the west (Ganghwa, Incheon, Asan, Gunsan), the pollution levels of the 3 new antifouling agents were higher compared with the butyltin compounds. The average value of $\sum$NEW in the western coastal areas in 2009 was 63.37 ng/L, indicating that the pollution levels of new antifouling agents were higher in the west sea than in the south (51.15 ng/L) and east seas (18.06 ng/L). In particular, chlorothalonil exceeded the detection limit in all western coastal areas. However, the average $\sum$BTs in

the west sea was only 7.02 ng Sn/L, lower than in the south and east seas. Based on this result, the contamination by antifouling agents has shifted from butyltin compounds to new antifouling agents in western coastal areas.

The Donghae harbor, in the east coastal area, is a clear example of a harbor that is influenced by military and coast guard ships. The D4 sector, which docks these ships, showed significantly higher pollution levels of butyltin compounds than other harbors in the east sea. Because military ships also docked in the S1 sector (Sokcho harbor), high concentrations of butyltin compounds were detected there.

Table 2
Distribution of butyltin compounds and new antifouling agents in the western, southern, and eastern seas.

		Chlorothalonil	Dichlofluanid	Irgarol 1051	$\sum$NEW	MBT	DBT	TBT	$\sum$BTs
West (*n* = 16)	Average (ng/L)	29.78	21.77	11.82	63.37	2.80	4.22	0.00	7.02
	Detection sites	16	11	6	16	5	3	0	5
	Frequency of detection (%)	100	69	38	100	31	19	0	31
South (*n* = 19)	Average (ng/L)	29.77	13.09	8.29	51.15	6.43	32.80	2.16	41.39
	Detection sites	19	14	10	19	10	13	3	14
	Frequency of detection (%)	100	73	52	100	52	68	15	73
East (*n* = 9)	Average (ng/L)	8.49	8.50	1.07	18.06	0.69	21.90	3.69	26.27
	Detection sites	7	7	1	8	1	4	2	4
	Frequency of detection (%)	79	78	11	89	11	44	22	44

Table 3
Traffic data of incoming vessels in harbors in from 2006 to 2009 (parentheses indicate the number of ships) [24].

| Years	2006	2007	2008	2009
Ganghwa	n.d.	n.d.	n.d.	n.d.
Sokcho	1,566,570 (692)	1,573,387 (643)	1,542,278 (526)	1,636,349 (602)
Donghae	15,081,088 (3,218)	15,553,056 (3,289)	17,108,103 (3,119)	17,572,595 (3,031)
Yeosu	15,644,639 (5,155)	19,345,360 (5,994)	27,106,048 (6,074)	40,329,990 (6,471)
Asan	65,758,355 (5,866)	70,421,428 (6,419)	77,517,894 (6,877)	75,704,669 (7,527)
Busan	363,598,204 (50,385)	395,128,596 (51,395)	416,338,349 (57,979)	425,536,329 (50,012)
Masan	32,083,510 (9,644)	36,826,755 (10,409)	37,920,902 (11,307)	35,872,731 (11,639)
Incheon	146,382,925 (20,979)	153,396,146 (21,694)	156,136,776 (20,738)	154,196,323 (19,997)
Ulsan	166,176,617 (25,992)	174,406,756 (27,904)	175,595,165 (27,462)	173,381,107 (25,412)
Gunsan	33,545,567 (4,173)	33,770,206 (4,265)	33,494,213 (4,394)	36,518,623 (4,623)

n.d.: no data; unit: tons.
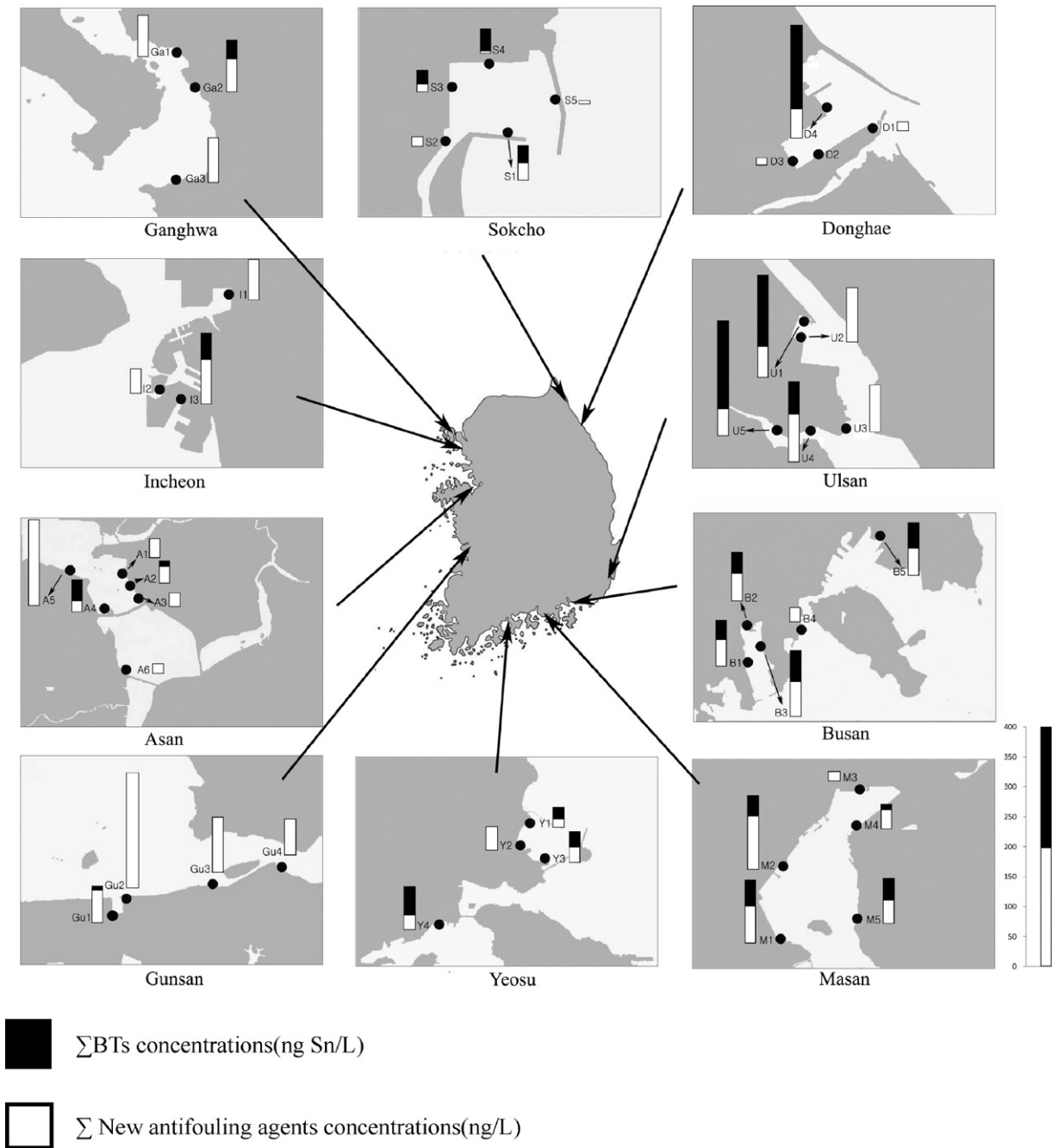
Fig. 3. Distribution of antifouling agents throughout major ports in Korea.

However, in the S3 and S4 sectors, where these ships do not dock, butyltin compounds were also detected. It is difficult to conclude that the butyltin compounds from the S1 area diffused to and polluted other areas of Sokcho. This finding might have been caused by illegal use of butyltin compounds. As shown in Table 2, the average concentration of $\sum$BTs in the eastern coastal areas was 26.27 ng, higher than in the west. Moreover, the frequency of detection of harbors in eastern coastal areas was 44%, higher than the 31% rate of the west. Thus, we conclude that eastern coastal areas experience more severe pollution of butyltin compounds compared with other coastal areas.

In the southern coastal area, which contains the biggest ports in Korea (Yeosu, Masan, Busan, Ulsan), higher concentrations of new antifouling agents, as well as butyltin compounds, were detected. The average concentration of $\sum$BTs was 41.39 ng Sn/L, and the fre-

quency of detection was 73%, indicating that the pollution level in southern coastal areas was significantly higher than in the western or eastern seas. In particular, the Y4 sector in Yeosu, where military and coast guard ships are docked, had high concentrations of butyltin compounds. However, in the areas where non-commercial ships were not docked, such as Busan (B1, B2, and B3), Ulsan (U1), and Masan (M1, M2, and M5), high concentrations of butyltin compounds were observed. In these areas, illegal use of TBT might have occurred, requiring a detailed study.

3.4. Factors that affect pollution by antifouling agents

In southern coastal areas, including big harbors, high concentrations of butyltin compounds as well as new antifouling agents were detected simultaneously. This phenomenon can be explained

by 3 reasons. First, because large ships were often docked in big harbors, the degree of pollution was severe due to the amounts of ballast that were discharged. Some reported that the pollution by ballasts was different, depending on the antifouling agents used on each ship [23]. Therefore, big harbors should concurrently investigate the butyltin compounds that have been used in the past, as well as new antifouling agents that are applied on new ships.

Second, the topographical characteristics can be considered. As shown in Fig. 3, the southern coast lines are much more complex than the western and eastern lines. This feature can act as a barrier against the circulation of seawater, thus allowing pollutants to accumulate in this region. Therefore, this property could be another reason why pollution levels are higher in the south than in the east and west.

Third, because the primary source of pollution of antifouling agents is ships, the size and number of ships that enter a harbor have a large effect on the pollution levels in that harbor. In order to evaluate this relationship, the size and number of incoming ships the harbors accommodate were compared with antifouling agent concentration levels. The possibility for errors in the data, however, still exists. For example, when a mother vessel and smaller feeder vessels enter the harbor simultaneously, only the mother vessel is counted. Also, among 10 harbors, Ganghwa is a very small harbor that does not have any traffic data. From 2006 to 2009, the size and number of ships in each area increased on the whole, and it was expected that the contamination of antifouling agents due to ships would continue to increase (Table 3) [24]. Our data show that the size of the ships that dock in major harbors in Korea is between 1000 and 60,000 tons. Among these harbors, Ulsan experiences severe pollution and has the highest traffic from ships as large as 100,000 tons, resulting in higher pollution levels. For Sokcho, a fishery harbor, the majority of its traffic is from ships smaller than 1000 tons and has less traffic and is smaller than other harbors. Donghae is similar to Sokcho, but the average size of its ships is slightly larger than ships in Sokcho (1000–20,000 tons) (Table 4).

The size and number of ships in harbors were compared with the average antifouling agent levels ($\sum$BTs and $\sum$NEW) in harbors. There was no close relationship between them. As a function of total tons (product of ship size and number) in the harbors, the concentrations of butyltin compounds did not increase, because butyltin compounds were not used in every harbor. In contrast, for new antifouling agents, as the total tons increased, so did the pollution level, especially in Sokcho, Donghae, Yeosu, Asan, Incheon, and Ulsan.

However, the remaining 3 harbors had slightly different results. Because Masan and Gunsan had low levels of traffic, a high concentration of new antifouling agents was detected; Busan had high traffic levels and low concentrations. Because Masan is in the shape of a bottle gourd, the pollutants tend to become trapped and accumulate. Thus, even with a low discharge rate, the pollution level in this harbor may be high (see Fig. 3).

Due to these regional characteristics, many other studies are underway for materials other than antifouling agents [25]. Moreover, the result from Gunsan may be affected by the ballast that is discharged from various ships. Conversely, Busan had low pollution concentrations, even with its high traffic levels, due to the dilution effects of fast currents of seawater. In spite of some exceptions, the number and size of ships have significant effects on the concentrations of new antifouling agents.

TBT is banned in many countries and conventions. It was expected that the ban would make the coastal environment clean, but this is still being argued. The arguments particularly focus on the use of TBT in developing nations without any regulation, on the organotin-based compounds being sold in the market, and on

Table 4
Traffic data of incoming vessels in harbors in 2008 (2008. 1.1–12.31) (parentheses indicate the number of ships) [24].

Ship size	0–1000 tons	1,000–20,000 tons	20,000–60,000 tons	60,000–100,000 tons	>100,000 tons	Sum	Average concentration $\sum$NEW	$\sum$BTs
Ganghwa	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60.03	9.31
Sokcho	76,605 (410)	1,465,673 (116)				1,542,278 (526)	15.87	18.29
Donghae	1,054,123 (1289)	8,330,043 (1567)	7,723,937 (263)			17,108,103 (3,119)	20.81	36.25
Yeosu	1,485,821 (4709)	4,704,143 (986)	10,332,725 (258)	6,644,125 (94)	3,939,234 (27)	27,106,048 (6,074)	28.66	23.99
Asan	1,992,651 (2133)	24,521,523 (3,816)	28,003,261 (696)	11,812,907 (138)	11,187,552 (94)	77,517,894 (6,877)	39.43	6.38
Busan	8,560,472 (27,406)	132,605,398 (24,679)	177,725,915 (4,649)	92,203,198 (1198)	5,243,366 (47)	416,338,349 (57,979)	46.52	33.49
Masan	2,850,082 (5,606)	21,671,279 (5,388)	11,150,444 (280)	2,249,097 (33)		37,920,902 (11,307)	51.45	25.21
Incheon	15,984,533 (8,596)	59,476,526 (10,298)	54,940,305 (1573)	16,163,945 (189)	9,571,467 (82)	156,136,776 (20,738)	54.43	12.91
Ulsan	6,984,036 (12,621)	54,288,940 (12,520)	74,265,490 (2032)	3,592,528 (51)	36,464,171 (238)	175,595,165 (27,462)	73.45	79.41
Gunsan	1,337,547 (1617)	11,757,217 (2,295)	17,395,494 (437)	2,893,414 (44)	110,541 (1)	33,494,213 (4,394)	108.49	1.84

n.d.: no data.

the lack of stability of the new antifouling agents [26]. The results of this study also appeared the illegal use of TBT in some harbors, and showed that the concentrations of the new antifouling agents, whose stability has not been verified, have been increasing after the banning of TBT. Therefore, TBT and the new antifouling agents must be continuously monitored, and the stability of alternative compounds must be verified.

4. Conclusions

The change in concentrations of butyltin compounds and 3 new antifouling agents was measured before and after the ban of TBT. The pollution by butyltin compounds has decreased while pollution by the 3 new antifouling agents increased between 2006 and 2009. Concentrations of the 3 new agents increased from 2006 to 2009, especially in harbors near agricultural areas. Butyltin compounds decreased overall in concentration; however, high concentrations were measured at harbors where military and coast guard ships were docked, as well as in big harbors in the southern and eastern seas. For the new antifouling agents, higher concentrations were detected in the west and south coastal areas. In conclusion, the coastal environment of the south sea is suffering heavily from both butyltin compounds and new antifouling agents. The pollution is affected by regional characteristics of the southern coast and the numbers and sizes of ships.

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