

한국연안의 갯벌 중에 유기주석화합물 및 새로운 방오도료제의 분석

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Analysis of Butyltin Compounds and New Antifouling Agents in the Southwestern Korean Tidal Flats

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요 약

유기주석화합물의 사용금지과 새로운 방오도료제의 사용으로 한국의 연안 환경은 매우 많은 변화를 겪었다. 1998년도에 측정된 서남해안 갯벌이 있는 동일한 지역(8지역) 기준으로 하여 유기주석화합물 및 새로운 방오도료제의 농도를 8지역에 주변까지 포함하여 총 39지점을 2006년도에 측정하였다. 2006년도의 TBT의 농도는 인천(It1)을 제외한 대부분의 지역에서 1998년에 비해 상당히 감소되었다. 제주도(Jt2), 목포(MOt4) 그리고 순천(SUt3)에서는 검출한계 이하로 검출되었다. 이것은 2003년 한국내에서 TBT화합물의 사용금지에 기인한 결과로 예측 할 수 있다. 하지만 한국의 대부분의 샘플링 지역에서 새로운 방오도료제인 Irgarol 1051, Dichlofluanid과 Chlorothalonil 이 검출 되었다. 이 중 특히 Irgarol 1051은 한국 연안에서 높은 농도로 검출 되었다. 제주도 (Jt4)에서는 Irgarol 1051이 159.45 ng g⁻¹(dry wt)로 검출되어 측정지점 중 가장 높게 검출이 되었다. 이 결과로 볼 때 2003년을 기점으로 한국 연안에서의 TBT 화합물은 점진적으로 감소 추세에 있고, 새로운 방오도료제가 쉽게 검출됨을 알 수 있었다.

Abstract – The prohibition of usage of tributyltin (TBT) compounds and the legal usage of new antifouling agents have changed the Korean costal environments in recent. 39 sampling sites of southwestern tidal flats were chosen in order to investigate the concentration of antifouling agents, and results in 2006 were compared with previous results in 1998. The concentrations of TBT compounds in most of sites except Incheon (It1) have been drastically decreased. Interestingly, In Jebudo (Jt2), Mokpo(MOt4) and Suncheon(SUt3) sites were detected as below the limit of detection and it is because of the legal restriction of TBT compounds. However, in most of the sampling sites in Korea, new antifouling agents, viz. Irgarol 1051, Dichlofluanid and Chlorothalonil, were detected. In particular, Irgarol 1051 was detected with high concentrations. In Jebudo (Jt4), a high concentration of Irgarol 1051 of 159.45 ng g⁻¹(dry wt) was detected. We were able to observe that the concentration of TBT compounds are has gradually been reduced whereas the new major antifouling agents are easily detected in most Korean tidal flats.

Keywords: Irgarol 1051(이르가롤 1051), Chlorothalonil(크로로타로닐), Dichlofluanid(디크로프루아니드), Butyltin compound(부틸주석화합물), Tidal flat(갯벌), Korea(한국)

1. INTRODUCTION

The attachment of organisms to the surface of a ship results in the reducing the speed and the corrosion of its surface. This natural damage has been protected by painting the antifouling agents to the surface of ship (Beech *et al.* [2004]). Antifouling technology has been intensively studied after the first patent by William Beale in 1625 (Chambers *et al.* [2006]). Tributyltin (TBT) compound was firstly reported as an antifouling agent in 1976 and it has since been widely used. Antifouling paints previously consisted of self-polishing copolymers (SPCs) in which the TBT functional group was attached to acryl resin exhibiting hydrophobic properties. However, the TBT in the resin is released into the sea in the form of TBTO (tributyltin oxide) exhibiting hydrophilic properties that are easily resolved in seawater. Because the detachment of TBTO occurs on the surface of the ship, and the resulting hydrophobic character of resin is advantageous to maintain the flat surface. So, the painting of TBT on the surface of the ship give rise to the effect of smoothing and finally toxicity of TBT (Chambers *et al.* [2006]). The high toxicity of TBT reduces the harvest of shellfish and, consequently, the International Marine Organization (IMO) and Korea government prohibited the application of TBT paints in 2003.

The usage of TBT was legally prohibited in Europe earlier than other countries. Starting from the restriction of TBT usage on small boats (<25 m) in 1987, the legal prohibition has become prevalent all over the European community (Stewart [1996]). In 2003, the commission directive 202/62/EC (EU commission, 2002) implying the restriction of usage of all organotin compounds in antifouling preparations became effective. After the legal restriction of TBT in 1998, the TBT concentration of the Elbe river in Germany has been actually reduced from the range of 10-570 ng/L in 1993 to the range of 2-230 ng/L in 2003 (Rudel *et al.* [2007]). Similar studies implying the effect of prohibition of TBT in Korea has accomplished for Korea tidal flats (Lee *et al.* [2000]) and compared with current studies.

After the restriction of TBT, ca 18 kinds of new antifouling agents are widely used throughout the world nowadays. Three major new antifouling agents were selected to determine the concentration in Korea coastal environment in this experiment. Even if new antifouling agents are made with low toxicity, their nature makes it difficult to entirely remove

their toxicity. Therefore, understanding the toxicity and chemical properties of these new antifouling agents are very important. In the case of copper based antifouling agents, the increased tolerance has been reported for a select group of macrophytes (Voulvoulis *et al.* [2002]) and booster biocides were used. Irgarol 1051 was the first booster biocide. In France, Irgarol 1051 was first determined at a concentration of 1,700 ng/L in sediment (Readman *et al.* [1993]). Because Irgarol 1051 has a cyclopropyl group and tert-butyl group having hydrophobic properties, therefore, it is accumulated more readily in sediment than in seawater. Irgarol 1051 is known to inhibit the photosynthetic electron transport in chloroplasts and this action that can occur at concentrations lower than 1 mg/L (De Noylles *et al.* [1981]). The use of Irgarol 1051 has been regulated by the UK health and safety Executive (Chesworth *et al.* [2004], Lambert *et al.* [2006]) and restricted to application on ships greater than 25 m in length. The hydrolytic degradation rate of Dichlofluanid is known to be very high because of a half life in seawater at various temperatures of a few hours. Based on its high degradation rate, no accumulation of Dichlofluanid in sediment is to be expected (Thomas *et al.* [2002]). Chlorothalonil has also been used as a biocide carrying 30-200 days of a half-life and toxicity (Zmillet *et al.* [1998], Caux *et al.* [1996]). Regular monitoring of these new antifouling agents are necessary to verify their toxicity and bioaccumulation.

This study is quite meaningful in that we can firstly compare the concentrations of butyltin compounds between 1998 and 2006 after legal restriction, and secondly, in that we were able to investigate the concentrations of the new antifouling agents appeared in the Korean coasts. The detail instrumental analyses of 39 sites in Korean southwestern tidal flats for the measurement of concentration of antifouling agents were carried out, and current results were compared with previous results in 1998.

2. EXPERIMENTAL

2.1 Chemicals

Dichlofluanid (99%) and Chlorothalonil (98%) were purchased from SUPELCO. Irgarol 1051 was purchased from Ciba-Geigy (UK). The internal standard, 9-Bromoanthracene was purchased from Aldrich. HPLC grade toluene was obtained from J.T Baker. Dibutyltindichloride (DBT, 96%) and Tributyltin chloride (TBT, 96%) were purchased from

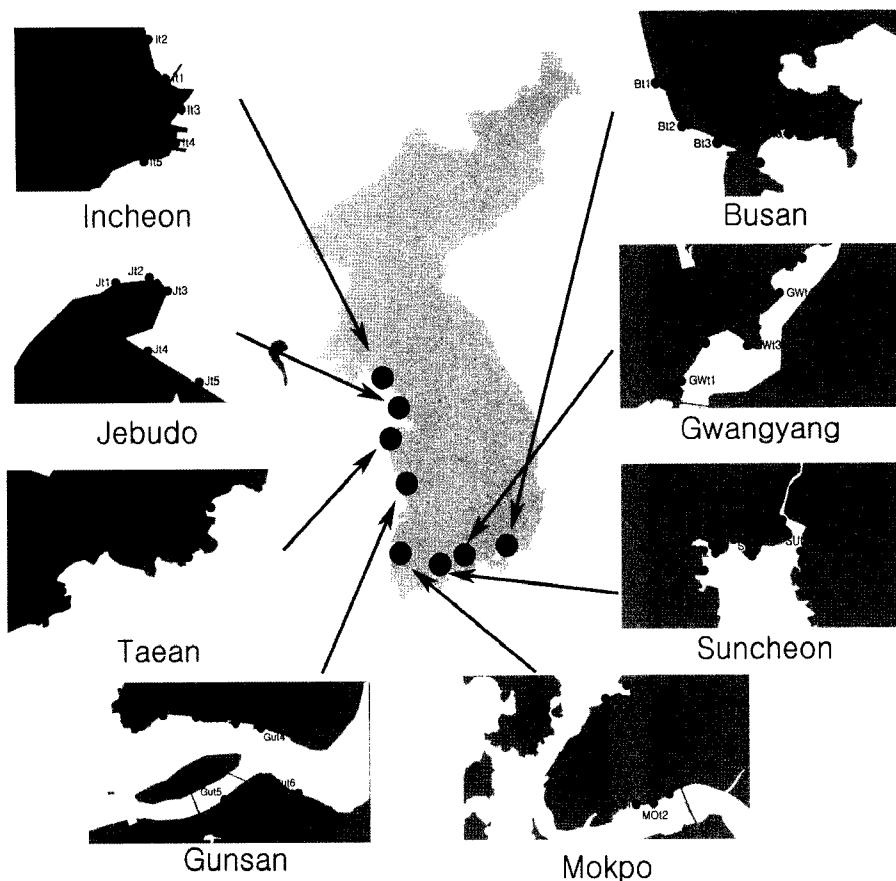


Fig. 1. Map of the sampling locations of the tidal flats along the Korean coast (the 8 main points).

Aldrich Chemical, Inc., Triethyltinchloride (TET, 98%) from Merck, and Monobutyltintrichloride (MBT, 95%) were purchased from Johnson Mattery Alfa Products. These standard materials were used without further purification. Methanolic stock solutions containing 1,000 ppm of tin were prepared monthly in a 25 ml of volumetric flask and stored at 4 °C. Working solutions were prepared daily from this stock solution. Sodium tetraethylborate was obtained from Aldrich. Solutions were prepared daily by dissolving 0.2 g in 10 ml of deionized water. Methanol and hexane of HPLC grade were obtained from Fisher.

2.2 Sampling sites

The tidal flats in Korea are mainly found on the west and south coasts. Therefore, the sampling sites in this experiment were confined mainly to the tidal flats of the west and south coasts (Fig. 1, Table 1). In order to accurately compare the butyltin compound concentrations to the data obtained in 1998, samples for the new tests were taken from the same sample sites as those used for the 1998 tests. The sites of the tidal flats were classified into three types. First, those tidal flats located in the harbor of anchoring

fishery ships, which are directly affected by the antifouling agents. Second, It4 in Incheon and GUt4 in Gunsan which both have small repair shipyards and would be expected to be highly contaminated by antifouling agents. Third, general tidal flat areas where many people gather shellfish. In total, 39 samples were obtained from the fishing harbor (sampling points 12), small shipyard (sampling points 2), and farm (sampling points 25) (Table 1 and Fig. 1). Sampling was carried out between August 19th, 2006 and August 22th, 2006.

2.3 Extraction of TBT and New Antifouling Agents

The samples collected from the tidal flats were dried in an 80 °C oven, and pulverized using a rubber hammer. 5 g of the sample, 20 ml of concentrated acetic acid and triethyltin chloride (TET), an internal standard, were transferred to the Teflon container of a microwave system (MARS5) made by CEM Co. Each sample was inserted into a microwave operating at 600 W, 100 °C for 4 min. The sample was then cooled to room temperature and centrifuged for 5 min at 4000 rpm. Then the upper transparent solution was transferred to a 100 ml volumetric flask, and 25 ml of NaOH (20 g/50 ml), 1 ml of sodium tetraethylborate and 1 ml of n-Hexane were added. After vigorous stirring the

Table 1. Location of the sampling points and classification of the tidal flats.

Site	Latitude °N	Longitude °E	Date	Classification	
Incheon	It1	37°29'31.78"	126°34'48.50"	2006.8.19	Fishery harbor
	It2	37°2'943.15"	126°34'47.39"	2006.8.19	Fishery harbor
	It3	37°29'25.80"	126°34'55.16"	2006.8.19	Fishery harbor
	It4	37°29'23.16"	126°34'54.36"	2006.8.19	Small shipyard
	It5	37°29'21.42"	126°34'49.67"	2006.8.19	General tidal flat
Jebudo	Jt1	37°10'40.56"	126°37'09.61"	2006.8.19	General tidal flat
	Jt2	37°10'42.50"	126°37'14.11"	2006.8.19	Fishery harbor
	Jt3	37°10'41.44"	126°37'18.43"	2006.8.19	General tidal flat
	Jt4	37°10'45.28"	126°37'23.89"	2006.8.19	General tidal flat
	Jt5	37°10'32.06"	126°37'31.73"	2006.8.19	General tidal flat
Taeon	Tt1	36°42'01.12"	126°13'52.15"	2006.8.22	General tidal flat
	Tt2	36°41'42.75"	126°13'38.07"	2006.8.22	Fishery harbor
	Tt3	36°41'25.42"	126°12'32.42"	2006.8.22	Fishery harbor
Gunsan	GUt1	36°00'31.37"	126°40'33.05"	2006.8.20	General tidal flat (estuary)
	GUt2	36°00'28.32"	126°41'15.10"	2006.8.20	General tidal flat (estuary)
	GUt3	36°00'27.09"	126°41'44.67"	2006.8.20	Fishery harbor (estuary)
	GUt4	36°00'19.01"	126°42'17.86"	2006.8.20	Small shipyard (estuary)
	GUt5	35°59'21.96"	126°41'46.22"	2006.8.20	Fishery harbor (estuary)
	GUt6	35°59'33.06"	126°42'40.49"	2006.8.20	Fishery harbor (estuary)
Mokpo	MOt1	34°47'29.94"	126°25'18.21"	2006.8.21	General tidal flat
	MOt2	34°47'32.17"	126°24'49.85"	2006.8.21	General tidal flat
	MOt3	34°47'42.92"	126°25'58.55"	2006.8.21	General tidal flat
	MOt4	34°50'14.71"	126°23'34.96"	2006.8.21	General tidal flat
	MOt5	34°50'48.14"	126°24'29.72"	2006.8.21	General tidal flat
Suncheon	SUt1	34°52'13.71"	127°29'25.45"	2006.8.20	General tidal flat
	SUt2	34°52'29.60"	127°29'37.32"	2006.8.20	General tidal flat
	SUt3	34°52'27.68"	127°30'14.82"	2006.8.20	General tidal flat
	SUt4	34°52'50.90"	127°30'45.55"	2006.8.20	Fishery harbor
	SUt5	34°52'26.05"	127°31'02.39"	2006.8.20	General tidal flat
Gwangyang	GWt1	34°55'56.62"	127°41'59.02"	2006.8.20	General tidal flat (estuary)
	GWt2	34°56'10.41"	127°42'11.58"	2006.8.20	General tidal flat (estuary)
	GWt3	34°56'10.47"	127°42'37.11"	2006.8.20	General tidal flat (estuary)
	GWt4	34°56'29.97"	127°42'50.60"	2006.8.20	General tidal flat (estuary)
	GWt5	34°56'45.84"	127°43'04.73"	2006.8.20	General tidal flat (estuary)
Pusan	Bt1	35°03'23.61"	128°57'23.49"	2006.8.21	General tidal flat (estuary)
	Bt2	35°03'04.34"	128°57'31.32"	2006.8.21	General tidal flat (estuary)
	Bt3	35°02'47.66"	128°57'55.58"	2006.8.21	General tidal flat (estuary)
	Bt4	35°02'44.54"	128°58'12.28"	2006.8.21	Fishery harbor (estuary)
	Bt5	35°02'58.05"	128°58'27.35"	2006.8.21	Fishery harbor (estuary)

solution for 1 hour, the agitation was stopped and then the organic phase was transferred into a vial for injection into the GC-FPD.

3 g of the tidal flat powder and 20 ml of concentrated acetic acid, and 20 ml of deionized water were added to a teflon tube and spiked with 50 µl of the internal standard solution containing the 10 ppm of 9-bromoanthracene. The sample was inserted into a microwave oven operated at 1,200 W, 100 for 15 minutes. The sample was cooled down to ambient temperature and centrifuged for 5 minutes under

4,000 rpm. The upper transparent phase of solution was transferred to a 50 ml of volumetric flask and 1 ml of toluene was then added. After stirring for 1 hour, the agitation was stopped and the organic phase was transferred to a vial a sample and 3 µl of each aliquot was injected into GC-MS.

2.4 Instrumental Measurement

A Hewlett Packard 5890 II GC equipped with a HP 5970 mass selective detector and an Ultra-2 column crosslinked 5% phenyl-methylpolysiloxane with 50 m length, 0.2 mm *i.d.*,

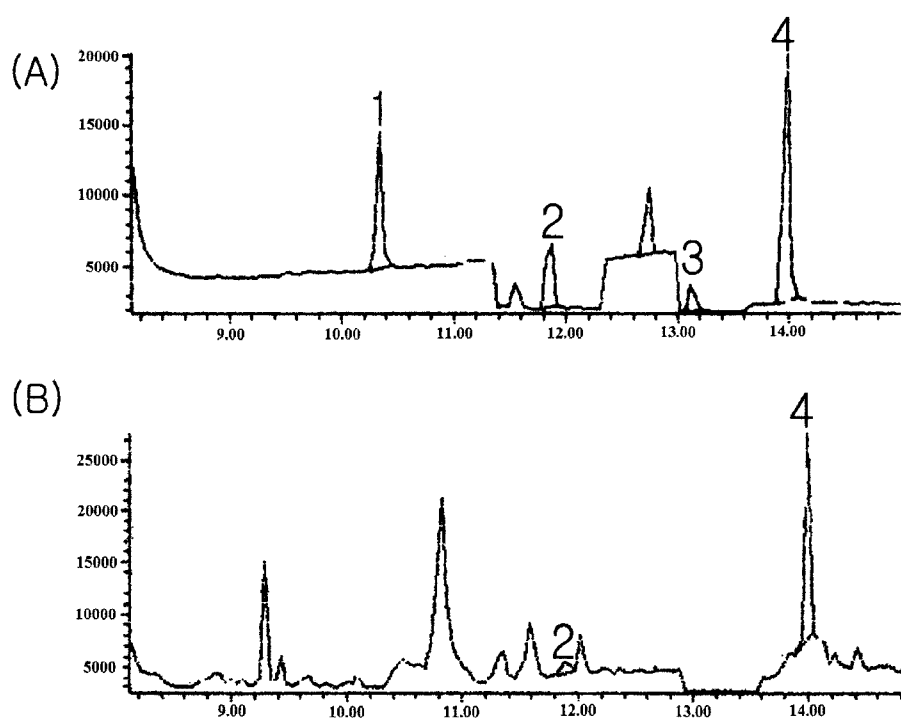


Fig. 2. GC-MS chromatogram of a tidal flat samples of standard 500 ng (A) and samples (Gunsan, GUt1, B) exhibiting the presence of (1) Chlorothalonil, (2) Dichlorofluanid, (3) Irgarol 1051 and (4) 9-Bromoanthraline.

film thickness 0.11 μm was used. After tuning the machine, the operating conditions were optimized as follows: injection volume, 3 μl ; injector temperature, 300 $^{\circ}\text{C}$; and split time, 80 sec. The oven temperature was programmed to stay at 105 $^{\circ}\text{C}$ for 1 min, to ramp up 25 $^{\circ}\text{C}/\text{min}$ up to 180 $^{\circ}\text{C}$. After staying for 1 min at this temperature, temperature was ramped 5 $^{\circ}\text{C}/\text{min}$ up to 230 $^{\circ}\text{C}$ and stayed for 20 min at this temperature. The transferline temperature was set to 280 $^{\circ}\text{C}$. Helium was used as carrier gas with a flow rate of 2 ml/min. The target and qualifier ions placed with the SIM descriptor are as follows: for Irgarol 1051, m/z 253, 238, 182 and 111; for Chlorothalonil, m/z 266, 229, 205 and 168; and for Dichlorofluanid m/z 332, 224, 167 and 154; for 9-Bromoanthracene m/z 256, 176, and 147. An electron multiplier of approximately 200 volts was used as a detector. The retention times were 10.349 min for Chlorothalonil, 11.871 min for Dichlorofluanid, 13.133 min for Irgarol 1051, and 13.980 min for internal standard of 9-bromoanthracene, respectively. The chromatograms of three different standards of new antifouling agents standard and actual sample are shown in Fig. 2.

For butyltin compounds, a Hewlett Packard 5890 II Gas Chromatography (GC) equipped with a split/splitless injector, fused silica capillary column (Ultra-1, 50 m, 0.32 mm, *i.d.*, film thickness 0.52 μm) and a flame photometry detector were used. It was used with a 610 nm cut off interference filter at a temperature of 250 $^{\circ}\text{C}$ by using hydrogen

and air flow rates of 45 and 35 psi/cm^2 respectively. The temperature of the injection port was set to 220 $^{\circ}\text{C}$ and helium of 20 psi/cm^2 was used as carrier gas using a splitless mode for 90 sec. The column temperature was programmed to stay at 60 $^{\circ}\text{C}$ for 2 min and heated up to 300 $^{\circ}\text{C}$ with a ramp of 30 $^{\circ}\text{C}/\text{min}$. The retention times were 10.107 min for internal standard, TET, 11.880 min for MBT, 13.560 min for DBT, and 15.107 min for TBT, respectively. The chromatograms of three different standards of butyltin compounds standard and actual sample are shown in Fig. 2. All calculations of butyltin compounds and new antifouling agents concentrations were performed by internal standard method.

2.5 Recovery Rates and Limits of Detections

For the recovery analysis, 100 ng Sn g^{-1} (dry wt) of the butyltin compounds and the new antifouling agents were added to seawater sample with the matrix. Replicate analyses of the spiked matrices (with $n=3$) revealed adequate precision with good recovery and repeatability, the results of which are shown in Table 2. The mean recoveries were 90.12% for MBT, 91.01% for DBT, 89.44% for TBT, 102.85% for Irgarol 1051, 87.51% for Dichlofluanid, and 95.13% for Chlorothalonil. The detection limits for Mono-, Di-, and Tributyltin, Irgarol 1051, Dichlofluanid and Chlorothalonil were 6.06 ng Sn g^{-1} (dry wt), 4.60 ng Sn g^{-1} (dry wt), 2.59 ng Sn g^{-1} (dry wt) 10.38 ng g^{-1} (dry wt), 5.64 ng g^{-1} (dry wt) and 11.16 ng g^{-1} (dry wt), respectively.

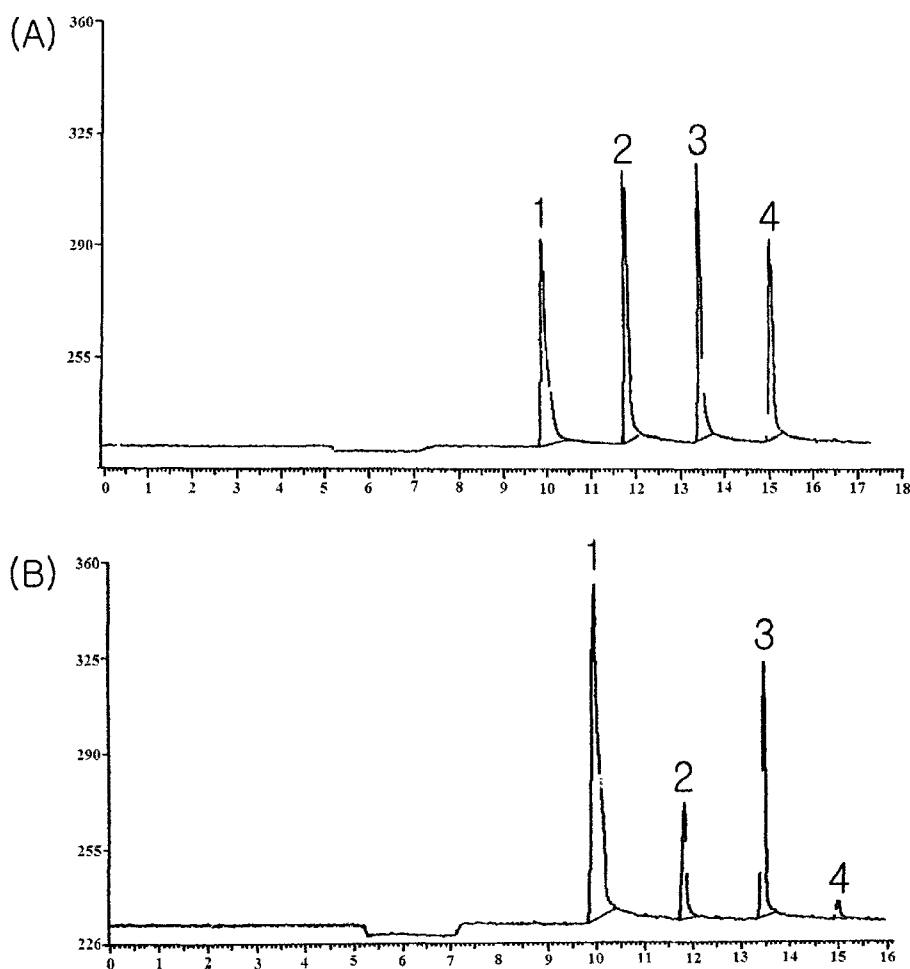


Fig. 3. GC-FPD chromatogram of a tidal flat samples of standard 500 ng (A) and samples (Jebudo, Jt4, B) exhibiting the presence of (1) TET, (2) MBT, (3)DBT and (4) TBT.

Table 2. Recovery and limit of detection of selected booster biocides from spiked tidal flat samples.(butyltin compounds: ng Sn g^{-1} (dry wt), new antifouling agents : ng g^{-1} (dry wt))

	Mean recovery (%)	RSD%(n=3)	LOD
MBT	90.12	1.25	6.06
DBT	91.01	2.57	4.60
TBT	89.44	2.61	2.59
Irgarol 1051	102.85	4.06	10.38
Dichlofluanid	87.51	4.48	5.64
Chlorothalonil	95.13	5.16	11.16

3. RESULTS

3.1 Retrospective Monitoring of Butyltin Compound Concentrations

Changes and comparisons of butyltin compounds are shown in Fig. 4 and Table 3 for the year of 1998 to 2006. The concentrations of butyltin compounds show that the TBT concentration is higher than that of MBT and DBT concentrations in 1998. After totally prohibition of TBT in 2003, butyltin compounds were reduced in 18 sampling sites out of 39 sites. The rest 21 sampling sites exhibit that

the concentration of the degradation product, MBT, was higher than TBT concentration. The result is explained by the fact that the butyltin compounds are decomposed and their concentrations are reduced compared with result of 1998.

In 1998, TBT, DBT and MBT concentrations in Incheon (It1) were measured to be 93.1, 7.1 and 0.8 ng Sn g^{-1} (dry wt), respectively. The composition percent of these TBT, DBT and MBT compounds were given to 92.2%, 7.2% and 0.8%, respectively. However, in 2006, TBT, DBT and MBT concentrations at same site were observed to 102.21, 73.87 and 65.63 ng Sn g^{-1} (dry wt), respectively. The corresponding composition percent were given to 42.3%, 30.6% and 27.2% respectively. The total amount of butyltin compounds concentration in 2006 was still higher than that in 1998, but the degradation ratio explains that TBT is under decomposed. In 1998, TBT, DBT and MBT concentrations were measured to be 25.0, 6.1 and 35.6 ng Sn g^{-1} (dry wt) at Gwangyang (GWt3) and the corresponding percentages were given to 37.5%, 9.1% and 53.4%, respectively. In 2006, TBT, DBT and MBT concentrations were measure to be 4.60, 37.18 and 10.51 ng Sn g^{-1} (dry wt) at same site

Table 3. Summarized data on the concentration of butyltin compounds in the Tidal flat samples taken in 1993 and 2006 (ng Sn g⁻¹ (dry wt))

Site	Year and analytes	1998			2006			Total butyltin compounds		Classification
		MBT	DBT	TBT	MBT	DBT	TBT	1998	2006	
Incheon	It1	0.8	7.1	93.1	65.63	73.87	102.21	101.0	241.71	Fishery harbor
	It2				N.D.	N.D.	N.D.		N.D.	Fishery harbor
	It3				71.37	42.96	56.52		170.86	Fishery harbor
	It4				60.39	35.16	46.16		141.71	Small shipyard
	It5				20.54	N.D.	N.D.		20.54	General tidal flat
	Average				43.59	30.40	40.98		114.97	
Jebudo	Jt1				N.D.	N.D.	N.D.		N.D.	General tidal flat
	Jt2	0.5	4.1	15.6	N.D.	N.D.	N.D.	20.2	N.D.	Fishery harbor
	Jt3				N.D.	N.D.	N.D.		N.D.	General tidal flat
	Jt4				14.26	32.75	22.60		69.62	General tidal flat
	Jt5				N.D.	N.D.	N.D.		N.D.	General tidal flat
	Average				2.85	6.55	4.52		13.92	
Taean	Tt1				N.D.	N.D.	18.72		18.72	General tidal flat
	Tt2	1.6	6.0	21.0	21.27	33.77	4.00	28.6	59.05	Fishery harbor
	Tt3				N.D.	28.88	N.D.		28.88	Fishery harbor
	Average				7.09	20.88	7.57		35.54	
Gunsan	GUt1				N.D.	N.D.	N.D.		N.D.	General tidal flat
	GUt2				N.D.	N.D.	N.D.		N.D.	General tidal flat
	GUt3				199.44	121.68	112.63		433.74	Fishery harbor
	GUt4	0.3	N.D.	11.7	32.89	N.D.	3.63	12.0	36.52	Small shipyard
	GUt5				9.95	7.31	12.47		29.73	Fishery harbor
	GUt6				59.30	119.95	47.28		226.53	Fishery harbor
	Average				50.26	41.49	29.34		121.09	
Mokpo	MOt1				N.D.	N.D.	N.D.		N.D.	General tidal flat
	MOt2				N.D.	39.53	3.02		42.55	General tidal flat
	MOt3				N.D.	N.D.	N.D.		N.D.	General tidal flat
	MOt4	2.4	7.2	46.2	N.D.	N.D.	N.D.	55.8	N.D.	General tidal flat
	MOt5				N.D.	N.D.	N.D.		N.D.	General tidal flat
	Average				0.00	7.91	0.60		8.51	
Suncheon	SUt1				N.D.	N.D.	N.D.		N.D.	General tidal flat
	SUt2				N.D.	N.D.	N.D.		N.D.	General tidal flat
	SUt3	0.8	1.4	45.9	N.D.	N.D.	N.D.	48.1	N.D.	General tidal flat
	SUt4				N.D.	N.D.	N.D.		N.D.	Fishery harbor
	SUt5				N.D.	N.D.	N.D.		N.D.	General tidal flat
	Average				0.00	0.00	0.00		0	
Gwangyang	GWt1				N.D.	43.38	4.84		48.22	General tidal flat
	GWt2				6.70	72.91	5.03		84.64	General tidal flat
	GWt3	35.6	6.1	25.0	10.51	37.18	4.60	66.7	52.30	General tidal flat
	GWt4				N.D.	12.61	N.D.		12.61	General tidal flat
	GWt5				90.65	39.05	N.D.		129.70	General tidal flat
	Average				21.57	41.03	2.89		65.49	
Pusan	Bt1				N.D.	N.D.	N.D.		N.D.	General tidal flat
	Bt2				N.D.	9.22	N.D.		9.22	General tidal flat
	Bt3	0.5	3.0	15.1	N.D.	N.D.	N.D.	18.6	N.D.	General tidal flat
	Bt4				N.D.	45.22	5.76		50.98	Fishery harbor
	Bt5				N.D.	9.55	10.43		19.98	Fishery harbor
	Average				0.00	12.80	3.24		16.04	

and the corresponding percentages were also given to 8.8%, 71.1% and 20.1%, respectively. In 1998, TBT, DBT and

MBT concentrations at Jebudo (Jt2) were measured to be 15.6, 4.1 and 0.5 ng Sn g⁻¹ (dry wt), respectively, but in

Table 4. Summarized data on the concentration of butyltin compounds and new antifouling agents in tidal flats in 2006.

Site	Analytes	New antifouling agents (ng g ⁻¹ (dry wt))				Butyltin compounds (ng Sn g ⁻¹ (dry wt))			
		Chlorothalonil	Dichlofluanid	Irgarol 1051	Total new anti	MBT	DBT	TBT	BTs
Incheon	It1	N.D.	13.46	N.D.	13.46	65.63	73.87	102.21	241.71
	It2	N.D.	19.15	131.12	150.27	N.D.	N.D.	N.D.	N.D.
	It3	N.D.	N.D.	42.31	42.31	71.37	42.96	56.52	170.86
	It4	N.D.	20.00	24.92	44.92	60.39	35.16	46.16	141.71
	It5	N.D.	N.D.	33.87	33.87	20.54	N.D.	N.D.	N.D.
Jebudo	Jt1	N.D.	N.D.	72.47	72.47	N.D.	N.D.	N.D.	N.D.
	Jt2	N.D.	N.D.	54.48	54.48	N.D.	N.D.	N.D.	N.D.
	Jt3	N.D.	N.D.	20.13	20.13	N.D.	N.D.	N.D.	N.D.
	Jt4	N.D.	N.D.	159.45	159.45	14.26	32.75	22.60	69.62
	Jt5	N.D.	17.19	67.16	84.35	N.D.	N.D.	N.D.	N.D.
Taeon	Tt1	N.D.	19.29	25.89	45.18	N.D.	N.D.	18.72	18.72
	Tt2	N.D.	59.79	N.D.	59.79	21.27	33.77	4.00	59.05
	Tt3	N.D.	23.06	88.29	111.35	N.D.	28.88	N.D.	28.88
Gunsan	GUt1	N.D.	22.86	N.D.	22.86	N.D.	N.D.	N.D.	N.D.
	GUt2	N.D.	37.11	114.88	151.99	N.D.	N.D.	N.D.	N.D.
	GUt3	N.D.	19.67	14.72	34.39	199.44	121.68	112.63	433.74
	GUt4	13.09	26.77	N.D.	39.86	32.89	N.D.	3.63	36.52
	GUt5	N.D.	28.49	84.94	113.43	9.95	7.31	12.47	29.73
	GUt6	N.D.	N.D.	N.D.	N.D.	59.30	119.95	47.28	226.53
Mokpo	MOt1	N.D.	N.D.	66.00	66	N.D.	N.D.	N.D.	N.D.
	MOt2	N.D.	10.76	43.90	54.66	N.D.	39.53	3.02	42.55
	MOt3	N.D.	9.64	26.03	35.67	N.D.	N.D.	N.D.	N.D.
	MOt4	N.D.	7.52	N.D.	7.52	N.D.	N.D.	N.D.	N.D.
	MOt5	N.D.	N.D.	44.96	44.96	N.D.	N.D.	N.D.	N.D.
Suncheon	SUt1	N.D.	13.89	39.58	53.47	N.D.	N.D.	N.D.	N.D.
	SUt2	N.D.	9.62	27.71	37.33	N.D.	N.D.	N.D.	N.D.
	SUt3	N.D.	10.77	37.89	48.66	N.D.	N.D.	N.D.	N.D.
	SUt4	N.D.	0.36	16.77	17.13	N.D.	N.D.	N.D.	N.D.
	SUt5	N.D.	10.39	31.81	42.2	N.D.	N.D.	N.D.	N.D.
Gwangyang	GWt1	N.D.	6.92	38.05	44.97	N.D.	43.38	4.84	48.22
	GWt2	N.D.	7.79	80.44	88.23	6.70	72.91	5.03	84.64
	GWt3	N.D.	N.D.	85.44	85.44	10.51	37.18	4.60	52.30
	GWt4	N.D.	N.D.	114.34	114.34	N.D.	12.61	N.D.	12.61
	GWt5	21.27	N.D.	N.D.	21.27	90.65	39.05	N.D.	129.70
Pusan	Bt1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Bt2	N.D.	N.D.	N.D.	N.D.	N.D.	9.22	N.D.	9.22
	Bt3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Bt4	N.D.	N.D.	N.D.	N.D.	N.D.	45.22	5.76	50.98
	Bt5	N.D.	N.D.	N.D.	N.D.	N.D.	9.55	10.43	19.98

2006 butyltin compounds were found as below the limit of detection Jebudo except for Jt4 also has same results. During sampling at the Jt4 site, some fishing boats were anchored, which is thought to be the reason for the detection of butyltin compounds at the site. Similar tendencies were observed at sampling sites of Taeon (Tt2), Gunsan (GUt4) and Pusan. All measurements of butyltin compounds were interestingly below the detection limits at any of the sites at Mokpo and Suncheon except for MOt2.

3.2 Concentration of New Antifouling Agents and Butyltin Compounds in Tidal Flats

In the analysis of the tidal flats in 2006, the total new antifouling agent concentration was increased and the total butyltin compounds concentration in Korea was decreased than result of 1998 as shown in Table 4. This implies that the usage of antifouling paints is being converted from TBT to new antifouling agents.

The total level of antifouling agent contamination can be

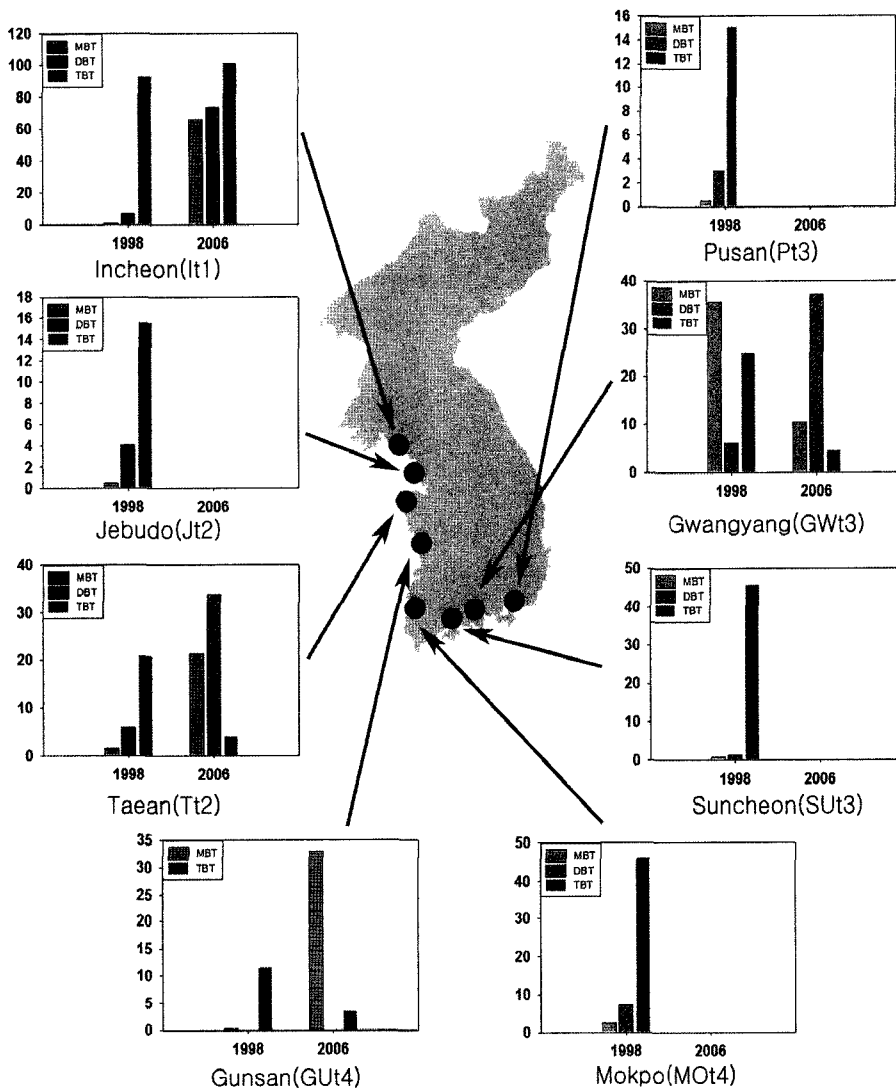


Fig. 4. Concentrations of butyltin (ng Sn g⁻¹(dry wt)) in tidal flat samples taken in years 1998 and 2006.

predicted by summarizing the concentrations of the eighteen different kinds of new antifouling agents. In our current studies, the total concentration of new antifouling agents is defined as the sum of three major antifouling agents for convenience. Among the new antifouling agents, Irgarol 1051 was detected in high concentrations in the Korean tidal flats. These results are consistent with the reason why hydrophobic Irgarol 1051 are well absorbed to sediment. (Kralik [1999]).

At It1, It3 and It4 in Incheon the total butyltin compound (Σ BTs) was highly measured because Incheon has a big harbor near the sampling site. In Jebudo, butyltin compounds were detected only at Jt4 where some boats were anchored near the sampling site. However, the new antifouling agents were detected at all of the sites in Jebudo. Irgarol 1051 concentration was especially high as 159.45 ng g⁻¹(dry wt) at Jt4. Butyltin compounds and the new antifouling agents

were detected simultaneously at Taean, although this site has a smaller harbor than the other sites. Especially, the concentration of Dichlofluanid (59.79 ng g⁻¹ (dry wt)) at Tt2 is one of the highest places in Korea. TBT concentration at GUt3 was particularly high as 112.63 ng Sn g⁻¹ (dry wt) The reason why Gusan has high concentration of TBT and new antifouling agents can be explained by the specific location of tidal flats. In Mokpo and Suncheon, the change from butyltin compounds to the new antifouling agents is clearly seen as in Fig. 3. Gwangyang is a special place having many steel manufacturers, and many vessels are also found in this area. Therefore, high concentrations of butyltin compounds and the new antifouling agents were detected at this site. Pusan is the foremost port in Korea and many ships are anchored at this site. However, the concentrations of butyltin compounds and the new antifouling agents were lower than those at the other sites. The reason

Table 5. Levels of the butyltin compounds(MBT, DBT and TBT) in the tidal flat samples reported in the literature (ng Sn g⁻¹(dry wt))

Location	MBT	DBT	TBT	Reference
Brazil	12 - 256	8 - 704	23 - 1388	Godoi <i>et al.</i> [2003]
Portuguese	<5.2 - 78	<2.5 - 18	<5.7 - 489	Diez <i>et al.</i> [2005]
United Kingdom	12-172	12-219	1-60	Scrimshaw <i>et al.</i> [2005]
France	-	-	4-158	Alzieu <i>et al.</i> [1998]
This experiment(2006)	N.D. - 199.44	N.D. - 121.68	N.D. - 112.63	

Table 6. Levels of the other antifouling agents, Irgarol 1051, Dichlofluanid, Chlorothalonil and Sea-Nine211, in the tidal flat samples reported in the literature

	Location	Tidal flat (ng g ⁻¹ (dry wt))	Reference
Irgarol 1051	North sea(Germany)	3-25	Biselli <i>et al.</i> [1998]
	Baltic sea(Germany)	24-220	Biselli <i>et al.</i> [1998]
	Blackwater Estuary(UK)	3.3-222	Voulvoulis <i>et al.</i> [2000]
	This experiment	N.D. - 159.45	
Dichlofluanid	Thessaloniki	N.D. - 65	Albanis <i>et al.</i> [2002]
	This experiment	N.D. - 59.79	
Chlorothalonil	Blackwater Essex(UK)	16.0-34.3	Voulvoulis <i>et al.</i> [2000]
	This experiment	N.D. - 21.27	

for this is the tidal flat characteristics of Pusan. This is characteristic point arisen from the particle size of the tidal flat in Pusan. Pusan tidal flat is classified by sand tidal flat (estuary). Because fine particles have much more surface area than that bigger size particles do, they are more capable of adsorbing pollutants (Kralik [1999]). We expect that the absorption of the new antifouling agent arising from the surface area is dependent on the size of particles.

3.3 Comparisons with Other Results

Comparisons of results for tidal flat are described as follow. Because there are not many tidal flats in other countries to investigate, most researches have been focused on the sediment containing the soil on the bottom of the harbor. In this experiment the butyltin compounds in Korea were observed with a certain concentration range of N.D.-199.44 ng Sn g⁻¹ (dry wt) for MBT, N.D.-121.68 ng Sn g⁻¹ (dry wt) for DBT, and N.D.-112.63 ng Sn g⁻¹ (dry wt) for TBT. These results were similar to those obtained for the sediment in the developed countries, England (MBT: 12-172 ng/g, DBT: 12-219 ng/g, TBT: 1-60 ng/g) and France (MBT: N.D., DBT: N.D., TBT: 4-158 ng/g) as in Table 5. Results of new antifouling agents are summarized in Table 6. The concentration of Irgarol 1051 in the Blackwater of estuary sediment in England was within N.D. - 222.3 ng/g, within N.D. - 15 ng/g in the North Sea sediment and within 2-80 ng/g in the Baltic sediment, but was within the N.D. -

159.45 ng g⁻¹ (dry wt) in Korea. The concentration of Irgarol 1051 in Korea is higher than in other countries. The Dichlofluanid concentration in Thessaloniki ranged from N.D. to 65 ng g⁻¹ (dry wt) and from N.D. - 59.79 ng g⁻¹ (dry wt) in Korea, respectively. The concentration of Dichlofluanid in Korea was in similar range to other countries. The concentration of Chlorothalonil in Blackwater of estuary sediment was ranged from 16.0 to 34.3 ng g⁻¹ (dry wt) and was N.D. - 21.27 ng g⁻¹ (dry wt) in Korea where is similar to that in other countries.

4. CONCLUSION

After the restriction of the usage of TBT compound in 2003, the coastal environment by antifouling paints in Korea has been considerably changed by Korea government regulation. Regarding the concentrations of butyltin compounds in tidal flats, half of 39 sampling sites were under detection limits, and this result indicates that the legal prohibition of butyltin compounds was successful in reducing the concentration of TBT. In addition, the observation that the DBT and MBT concentrations were higher than the TBT concentration in the rest of sampling sites implies that the degradation process of TBT compounds are in progress as in some developed countries. We were able to identify the appearance of new antifouling agents in the tidal flats in Korea. The considerable amount of Irgarol 1051 (ND-159.45 ng g⁻¹ (dry wt)) exhibiting hydrophobic properties so that

can be easily absorbed in tidal flats was found comparable to other advanced countries. Further monitoring of these new antifouling agents are necessary in order to improve the ecology of the coastal regions in Korea.

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