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Determination of the concentrations of alternative antifouling agents on the Korean coast

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ABSTRACT

Since the ban on tributyltin (TBT) in 2008, dozens of alternative antifouling agents have been used instead. Unfortunately, these alternative antifouling agents contain diverse toxic components, which have contaminated the coasts. From 2006 to 2013, the concentration of chlorothalonil, dichlofluanid, and Irgarol 1051 were monitored continuously, and their mean concentrations increased due to the increase in maritime cargo and consequent increase in the incoming and outgoing ships in harbors. An analysis of the sampling points according to harbor type showed that the contamination was more severe in fishing and big harbors, where there are more incoming and outgoing ships. A correlation analysis indicated a high correlation between chlorothalonil and dichlofluanid. Unlike Irgarol 1051, which is only used as an antifouling agent, the other two substances are used as agricultural chemicals as well, which could explain the high correlation. This study suggests that these alternative antifouling agents should be tracked continuously.

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1. Introduction

Coastal contamination due to antifouling agents has resulted in the destruction of the ecosystem due to a decrease in the populations of marine plants and animals. Since the ban of tributyltin (TBT) in 2008, due to TBT causing particularly high levels of damage, dozens of other antifouling agents with supposedly lower toxicity have been used (Lee et al., 2011). These alternative agents now have antifouling systems with different mechanisms than those that had TBT as the main component. Antifouling agents with a chemical system, instead of a physical system, are basically toxic and affect the marine environment in different ways. Therefore, many studies on their toxicity are currently underway (Fernández-Alba et al., 2002).

Several countries have been regulating Irgarol 1051 because of the toxicity that can occur at lower concentrations (1 µg/L) and long half-lives (200 days) (DeNoyelles et al., 1982). Therefore, the usage of Irgarol 1051 requires continuous observation. Dichlofluanid and chlorothalonil, important pesticides in agriculture, are widely used in Korea. The monitoring of these compounds has been continuously reported in reference to their effects on farming soil and rivers (Qu et al., 2015). However, these compounds, when used as antifouling substances, have also polluted marine environments. Dichlofluanid and chlorothalonil have been reported to have lower toxicity than other alternative antifouling

agents. Nevertheless, the mixed toxicity of these compounds with Irgarol 1051 was recently identified (DeLorenzo and Serrano, 2006).

Many alternative antifouling agents with chemical systems are based on pesticides for agricultural crops; some of which are used as the primary pesticides in Korea. The total use of agricultural chemicals in Korea is continuously decreasing (Statistics Korea, 2014). Such a trend was spawned by the improvement of farming methods, such as eco-friendly agriculture, and by strengthened agricultural product safety inspections. Despite the decrease in the use of agricultural chemicals, however, pesticide use still affects the environment through the water and soil systems.

Two of the alternative antifouling agents in this study, chlorothalonil and dichlofluanid, are also representative agricultural chemicals in Korea. Residual pesticide measurements in the major estuaries showed that the pesticides flowed along the rivers and affected the coasts (Cho et al., 2014).

The primary aim of this study was to measure the change in antifouling compounds used on the coast of Korea from 2006 to 2013. In addition, 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

HPLC-grade toluene was obtained from J.T. Baker (Center Valley, PA, USA). The dichlofluanid (99%) and chlorothalonil (98%) were purchased

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from SUPELCO (Bellefonte, PA, USA). The Irgarol 1051 was provided by Ciba-Geigy (Basel, Switzerland). The internal standard vinclozolin was supplied by Riedel-de Haën (Munich, Germany). The toluene stock solutions containing 1000 ppm were prepared weekly in a 25-mL volumetric flask and stored in a dark room at 4 °C. The working solutions were prepared daily from these stock solutions.

2.2. Sampling sites

Thirty-seven sampling sites were comprised of 13 fishery harbors, 18 big harbors, 4 harbors adjacent to agricultural areas, and 2 harbors in which coast guard and military vessels were docked (Table 1). The use of antifouling agents by small ships was investigated, because fishery harbors are ports with a high concentration of boats/ships <25 m in size.

On the other hand, fishing boats accounted for a small portion of the gross tonnage, but for a large portion in terms of their numbers. Big harbors near industrial areas were selected since the pollution from antifouling agents by large, continuously-entering and exiting ships was expected to be high. Harbors near agricultural areas were monitored because some alternative antifouling agents are also used as herbicides. The monitoring of antifouling compounds in the ports that docked coast guard and military vessels was also performed because they fell under the exception clause for non-commercial ships in the IMO's (International Maritime Organization) TBT ban regulation. Samples were taken from June 18th to 21th, 2006, from July 19th to 23th, 2009, and from Aug 11th to 15th, 2013. Two liters of seawater were drawn from a depth of 20 cm and stored in polyethylene (PE) bottles. All of the samples were protected by storage in a deep freezer (−20 °C). The number

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°56'50.99"	126°48'17.83"	F
	A3	36°58'58.28"	126°45'38.95"	A
	A4	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"	F
	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°04'19.94"	129°00'19.47"	B
	B3	35°04'52.80"	129°01'34.12"	B
	B4	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
Sokcho	U5	35°30'10.88"	129°22'01.91"	B
	S1	38°12'24.15"	128°35'54.07"	MC
	S2	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 and MC: Military Ship and Coast Guard Ship.

of sampling points in 2013 was lower than the 44 sampling points in 2009. The reasons for the decrease in sampling points were harbor re-modeling and the prohibition of entrance for security.

2.3. Extraction methods

A liquid–liquid extraction method was used to extract the alternative antifouling agents. Liquid–liquid extraction methods and SPE extraction methods could be used to extract the antifouling agents from seawater. SPE extraction has been used more often recently, but liquid–liquid extraction methods can be analyzed quickly without equipment. All of the samples were successively passed through a 0.45 µm pore size membrane filter (Advantec, Tokyo, Japan). 1 L of seawater was transferred to a volumetric flask, along with the 1.0 ppm internal standard (vinclozolin). Toluene (1.0 mL) was then added and stirred vigorously at 2000 rpm for 1 h in order to extract the agents. The agitation was stopped and the organic phase was transferred to a vial. Then, 3.0 µL of each aliquot was injected into the GC–MS.

2.4. Measurements on instruments

Analysis of Irgarol 1051, chlorothalonil and dichlofluanid was undertaken using a HP 5890 Gas chromatography with 5970 MSD and HP-5MS capillary column (crosslinked 5% phenyl-methylpolysiloxane with a 50 m length, 0.2 mm i.d., and 0.11 µm film thickness) in selected ion-monitoring mode (SIM). After tuning the machine, the operating conditions were optimized as follows: injector temperature: 250 °C and split time: 90 s. The oven temperature was programmed to be maintained at 70 °C for 2 min and then ramped at 20 °C/min to 120 °C. After holding for 1 min at 120 °C, the temperature was ramped at 30 °C/min to 230 °C, where the temperature 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 vinclozolin, *m/z* 285, 241, 212, and 187. An electron multiplier of 2600 V was used as the detector. The retention times were 21.1 min for chlorothalonil, 22.5 min for dichlofluanid, 25.2 min for vinclozolin (internal standard), and 28.4 min for Irgarol 1051.

2.5. Recovery rates and detection limits

In order to analyze the recovery, 100 ng/L of the alternative antifouling agent was added to the standard sample and the real seawater sample using a matrix. Replicate analyses of the spiked matrices ($n = 3$) confirmed adequate precision with good recovery and repeatability. The mean recoveries (RSD) were $75.63 \pm 1.95\%$ for Irgarol 1051, $105.46 \pm 3.54\%$ for dichlofluanid, and $101.86 \pm 3.76\%$ for chlorothalonil. The standard solution (1000 ppm) was newly prepared for every experiment when a calibration curve was drawn since the antifouling agents can degrade quickly. The calibration curves were evaluated in the range of 5, 10, 20, 50, and 100 ng/L, and they 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 4.23, 1.24, and 4.14 ng/L.

2.6. Statistical analysis

Statistical analyses were conducted to determine the diversity of measured values. The Spearman's correlation test was used as a statistical analysis method that is used when the sample size is small, or when it follows non-normality. After the test on normality, the Spearman's correlation test checked the significant correlations between the concentrations of three alternative antifouling agents in seawater. A

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