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Study on the New Antifouling Compounds in Korean Coasts

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Abstract After prohibition of use of organic tin compounds, new antifouling agents have been used as substitute paints. In 2009, this lab re-conducted the same research from 2006 that focused on concentrations of chlorothalonil, dichlofluanid, and Irgarol in the major bays of Korea, in order to assess changes in concentrations. Among the new antifouling agents detected in 2006, chlorothalonil, dichlofluanid, and Irgarol 1051 were detected up to 4.19, 61.69, and 23.80 ng/L, respectively. However, in 2009, up to 67.96, 74.79, and 67.64 ng/L were detected. Compared to 2006, there were apparent increases in the concentration of all three compounds in all areas where the research was conducted. These results indicate the need for further research regarding the hazards of these compounds.

Keywords Chlorothalonil · Dichlofluanid · Irgarol 1051 · Seawater · Korea coast

For the last few decades, the use of TBT has exerted negative influences upon the marine ecosystems along the coasts of Korea, such as imposex. Thus, in 2003, the Korean government and the IMO (International Maritime Organization) completely banned the use of TBT. This led to an anticipated increase in the use of new antifouling agents as alternatives to TBT (IMO 2001).

Approximately 20 types of new antifouling agents have been introduced worldwide; their collective and most significant benefit is a diminished toxicity relative to TBT. Nevertheless, since it is difficult to completely eliminate the toxicity of any antifouling agent because of its fundamental characteristics, continuous monitoring is necessary. For this research, chlorothalonil, dichlofluanid, and Irgarol 1051, three widely used antifouling agents, were studied.

Unlike butyltin compounds, each of the new antifouling agents possesses different toxicities and decomposition mechanisms; therefore, different approaches to each compound are required for complete chemical analysis. It has been reported that Irgarol 1051, a symmetrical triazine compound, interferes with the electronic movement within Photosystem-II and is highly toxic to marine organisms, yet less toxic to animals (Kem 1994).

Chlorothalonil and dichlofluanid have been commonly used as herbicides on crops, and their toxicity reported in a number of documents. In particular, chlorothalonil has been reported for its high toxicity toward fish and other aquatic invertebrates (Caux et al. 1996).

Even though new antifouling agents are less toxic than TBT, their toxicities can be amplified due to other factors. If the half-lives of these substances are long, a continual influence on the marine ecosystem is expected; therefore, an influence should be considered. Additionally, the toxicity of the products formed after degradation of the new antifouling agents should be considered as well.

Among the new antifouling agents that were studied, chlorothalonil and dichlofluanid possess very short half-lives, 4 weeks and 0.8 days, respectively (Motonaga et al. 1996; Thomas et al. 2002). However, Irgarol 1051 has a longer half-life of 100–200 days. Consequently, in Britain

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and Denmark, its use has been banned in pleasure crafts (Konstantinou 2006). Many countries across the world are conducting research on the pollution levels and toxicity of Irgarol 1051 (Liu et al. 1999). Since chlorothalonil and dichlofluanid have short half-lives, their concentration in the seawater is low in many regions. However, the degradation of these substances involves photodegradation as its basic mechanism, and if they are not degraded in the seawater, but rather absorbed into the sediment where there is no light, there can be a continuous and prolonged influence (Martinez et al. 2000).

Chlorothalonil, dichlofluanid, and Irgarol 1051 create degradation products that cause a numerous problems in marine ecology systems. Studies of their concentrations and toxicities have been reported. As a result, research on new antifouling agents for the aforementioned reasons are required (long half-lives and degradation products) (Hamwijk et al. 2005). In particular, this research is required to offer basic information about pollution along the coast of Korea.

To extract antifouling agents from seawater, liquid–liquid extraction methods and SPE extraction methods can be readily employed. Recently, SPE extraction methods have been used more frequently, but liquid–liquid extraction allows for quick analysis without equipment and as such, is also used widely. According to the research by Liu et al., there is no difference between the results of recovery tests using SPE extraction and liquid–liquid extraction. For this research herein, a liquid–liquid extraction method was employed (Liu et al. 1999).

To analyze new antifouling agents, various apparatus can be employed as each compound has different characteristics. Typically, GC-ECD is used for chlorothalonil and dichlofluanid and GC-NPD for Irgarol 1051; GC–MS was used since three compounds with different characteristics needed to be analyzed simultaneously (Chen et al. 2000; Ricardo et al. 2006).

The purposes of this research are the following: First, restudy and check the change in pollution levels in the same region in 2009, using the results of the study that reported the new antifouling agents in seawater in 2006; Second, check the spatial distribution of the pollution by the new antifouling agents in the Korean Peninsula since regulation in 2003 by averaging the results in 2006 and 2009.

Materials and Methods

Dichlofluanid (99%) and chlorothalonil (98%) were purchased from SUPELCO, Irgarol 1051 from Ciba–Geigy, and the internal standard, 9-bromoanthracene, from Aldrich. Toluene stock solutions were prepared weekly in a 25 mL volumetric flask and stored at 4°C. The 9-bromoanthracene was used by Okamure et al. as an internal standard to analyze the new antifouling agents and assessed to be stable (Okamura et al. 2003).

Seawater sampling was performed at small harbors (19 sites), big harbors (22 sites), and bays (four sites), among a total of 45 samples (Fig. 1). These included four sites where coast guard ships and military ships were anchored and four sites that included ports with industrial complexes. The substances that were the subject of this study were also used commonly as agricultural chemicals; therefore, four sites that accommodated ports close to fields and paddies were included. Sampling was done from June 18 to June 21 2006 and from July 19 to July 23, 2009. The 5.0 L of seawater was sampled from 20 cm below the surface of the ocean and placed in PE (polyethylene) bottles. All samples were stored at −20°C in a refrigerator.

For extractions and analysis, the same conditions as those employed in 2006, a liquid–liquid method and GC–MS conditions, were used again for consistency of results (Lee et al. 2008). For analysis recovery, 100 ng/L of the new antifouling agents were added to the standard sample and real seawater sample with a matrix. Replicate analysis of spiked matrices ($n = 3$) revealed adequate precision with good recovery and repeatability. The mean recoveries (RSD) were 73.55 ± 1.64% for Irgarol 1051, 93.83 ± 2.34% for dichlofluanid, and 120.28 ± 4.87% for chlorothalonil.

The standard solution (1,000 ppm) was newly made for every experiment when drawing a calibration curve, as the antifouling agents can degrade easily. The calibration curves were evaluated in the range of 5, 10, 20, 50, and 100 ng/L; all showed good linearity ($R^2 > 0.999$). Limit of detection was calculated using the regression analysis suggested by the EPA. The respective detection limits for chlorothalonil, dichlofluanid, and Irgarol 1051 were 5.52, 1.77, and 7.66 ng/L, respectively.

Results and Discussion

The summary of concentrations of chlorothalonil, dichlofluanid, and Irgarol 1051 that was analyzed in 2006 and 2009 is shown in Fig. 2 and Table 1. The concentration of the chlorothalonil measured in 2006 was ND–4.19 ng/L. Dichlofluanid had a concentration of ND–61.69 ng/L, and for Irgarol 1051 it was ND–23.80 ng/L (Lee et al. 2008). The concentration of chlorothalonil measured in 2009 was ND–67.96 ng/L, while for dichlofluanid it was ND–74.79 ng/L, and Irgarol 1051 it was ND–67.74 ng/L.

The concentration in all regions ($n = 45$) was checked yearly using the average value. The average value of chlorothalonil in 2006 was 0.99 ng/L, but increased to 24.65 ng/L in 2009. Dichlofluanid was 7.62 ng/L in 2006,

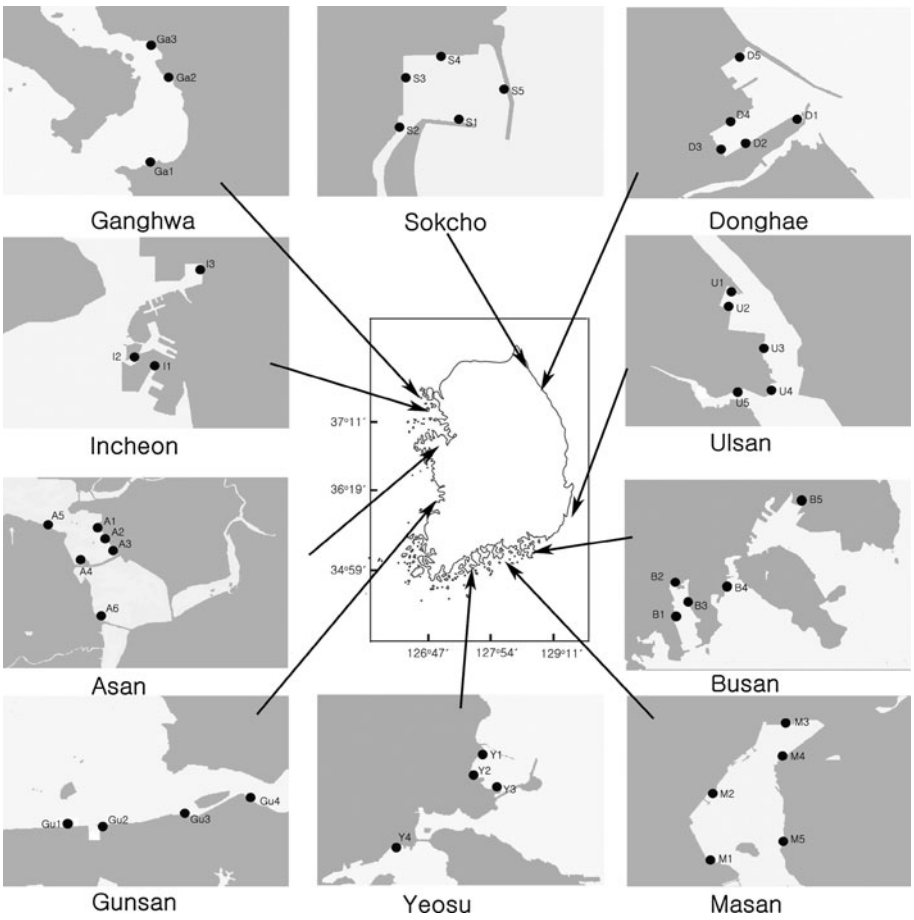

Fig. 1 Sampling sites of Seawater

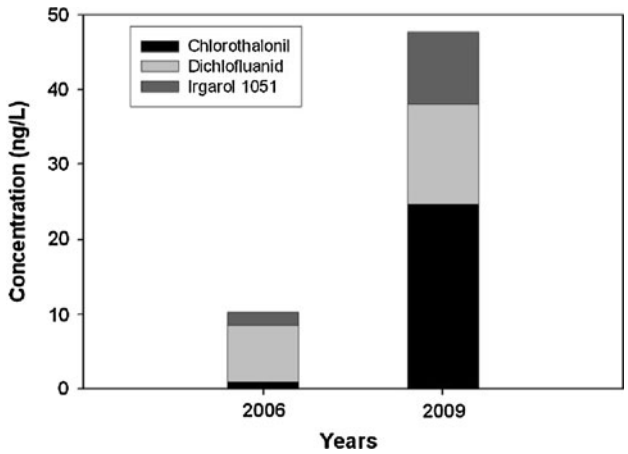

Fig. 2 Comparison of average concentrations by Year

but increased to 13.43 ng/L in 2009. The average value of Irgarol 1051 was 1.69 ng/L in 2006, but increased to 9.64 ng/L in 2009. All three substances increased from 2006 to 2009.

The average concentration in 2006 was lower than in 2009, seemingly because the test was conducted before residual prohibition on the surface of a ship in 2008 from the TBT regulation plan. It is therefore supposed that the use of new antifouling agents in 2006 was not high.

The frequency detection of each substance was also studied, indicating that the ratio of samples among all the samples that exceeded the detection limit. Frequency detection of chlorothalonil increased from 62% in 2006 to 98% in 2009, while Irgarol 1051 increased from 13% in 2006 to 73% in 2009. However, the frequency of detection of dichlofluanid decreased from 80% in 2006 to 73% in 2009, while its average concentration increased between 2006 and 2009. Accordingly, several deductions regarding the cause of the decrease in frequency detection were made.

First, when TBT was used as the main antifouling agent, the pollution level of all the antifouling agents was ascertained by researching the concentration of TBT. At present, approximately 20 antifouling agents besides TBT are in use, and in particular, the regions for this research are expected to be influenced by antifouling agents used in various countries around the world as there are many international ports there. As a result, obtaining information regarding the main antifouling agents in the sampling sites would prove capricious. It is thus expected that there are

Table 1 Summary of new antifouling agent concentrations in seawater from Korean coastal areas during 2006–2009

	Chlorothalonil		Dichlofluanid		Irgarol 1051	
	Range (Mean) (ng/L)	Frequency of detection (%)	Range (Mean) (ng/L)	Frequency of detection (%)	Range (Mean) (ng/L)	Frequency of detection (%)
2006 (n = 45) (Lee et al. 2008)	ND–4.19 (0.99)	62	ND–61.69 (7.62)	80	ND–23.80 (1.69)	13
2009 (n = 45)	ND–67.96 (24.65)	98	ND–74.79 (13.43)	73	ND–67.74 (9.64)	73

many ships that did not utilize dichlofluanid at the time of study, implying a reduction in detection of frequency.

Second, it may be due to the speed of degradation of dichlofluanid as its half-life is shown to be 0.8 days (Thomas et al. 2002). High concentrations of DMSA, a degradation product, can be detected as a result of the influence of this half-life. According to the study by Hamwijk et al. the amount of dichlofluanid detected was below the detection limit in the Greece seawater, but DMSA was detected (Hamwijk et al. 2005). It was also detected below the detection limit in some area, but it is possible that it went undetected because of fast degradation. Therefore, in order to determine the precise amount of dichlofluanid used, it is necessary to conduct a detailed study, such as a DMSA concentration study. Figure 2 shows a scale bar of the concentration of three compounds assessed, with the overall concentration dramatically increasing from 2006 to 2009.

Various patterns in pollution in each region were noted, which seemed to be caused by different characteristics of the regions and substances (antifouling agents). In 2006, the concentration of new antifouling agents was low in general, but high at some sampling points, mainly in large ports: D3 (Irgarol 1051, 23.80 ng/L) in the East Sea; U2 (dichlofluanid, 18.96 ng/L) in Ulsan; B2 (dichlofluanid 61.69 ng/L) in Busan; M4 (dichlofluanid, 27.31 ng/L) in Masan; Gu2 (dichlofluanid, 29.24 ng/L) in Gunsan. The concentration was not high at all sites, and new antifouling agents seem to be focused in the southern coast of Korea, indicating that the marine ecosystem in the Korean Peninsula was less influenced by new antifouling agents in 2006.

The result of the analysis in 2009 indicates high concentrations in all regions except Sokcho harbor and Donghae harbor. In 2009, the concentration of chlorothalonil was particularly very high in Ulsan, 67.96 ng/L in the U2 region. Large vessels are anchored at all times in this region, and these ships discharge large amounts of ballasts. No research was done on the pollution caused by ballasts containing new antifouling agents, but high concentrations of TBT were detected in docked ballast in other research (Hua and Liu 2007). If new antifouling agents were used in anchored ships, then the possibility of discharge in high concentrations should not be ruled out entirely.

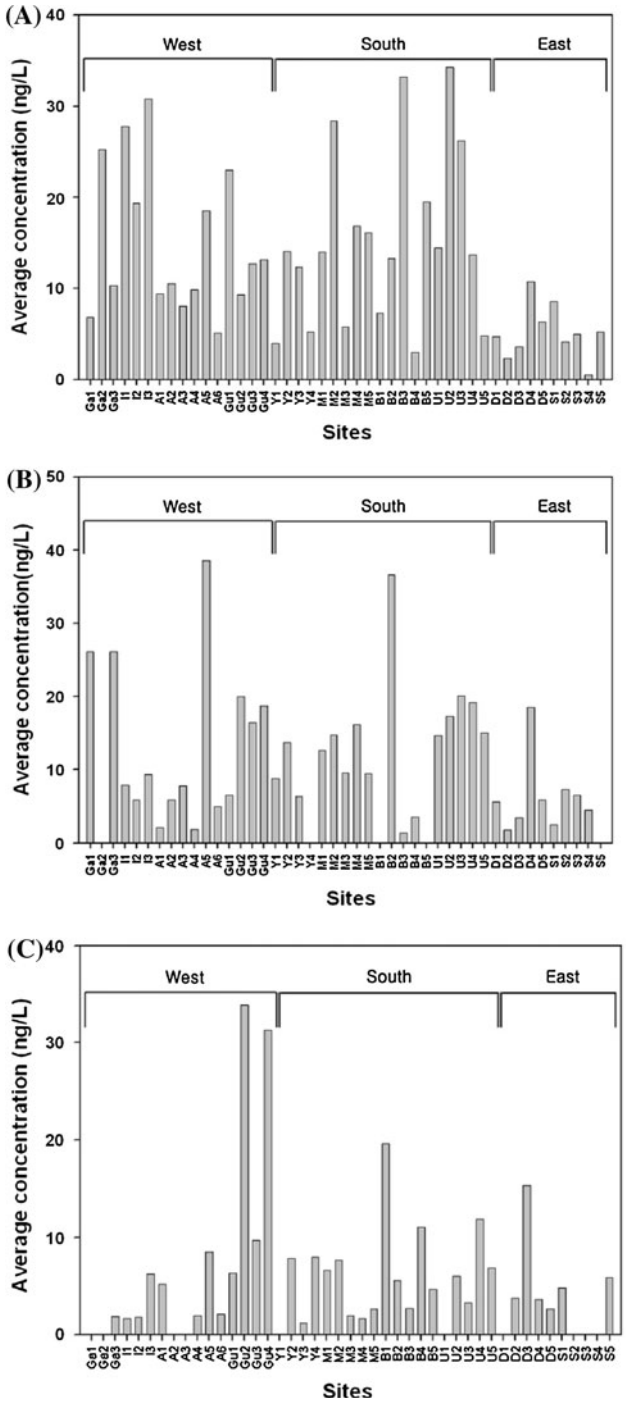

Fig. 3 Concentration of **a** chlorothalonil, **b** dichlofluanid and **c** Irgarol 1051, average of values in 2006 and 2009

Table 2 Levels of other antifouling agents such as Irgarol 1051, dichlofluanid, and chlorothalonil in seawater samples as reported in the literature

Chemicals	Sampling year	Country	Location	Description	Concentration (ng/L)	Ref.
Chlorothalonil	1998–1999	UK	Blackwater	Estuary	ND–1.38	(Voulvoulis et al. 2000)
	2002	Greece	The whole country	Port	ND–63	(Sakkas et al. 2002)
This exp.	2006–2009	Korea	The whole country	All kinds	ND–67.96	
Dichlofluanid	1998–1999	Spain	Mediterranean	Coast	ND–600	(Martinez et al. 2000)
	1998–1999	UK	Blackwater	Coast	ND–ND	(Voulvoulis et al. 2000)
					ND–668.2 ng/g (sediment)	
	1999	Greece	Piraeus	Port	ND–26	(Sakkas et al. 2002)
	2003	Greece	Chalkida	Shipyard	ND–ND	(Hamwijk et al. 2005)
					ND–36 ng/L (DMSA)	
This exp.	2006–2009	Korea	The whole country	All Kinds	ND–74.79	
Irgarol 1051	1999–2000	USA	Biscayne	Bay	ND–29.4	(Gardinali et al. 2002)
	2000	Netherlands		Coast	ND–70	(Lamoree et al. 2002)
	2002	Greece	Mytilene	Aegean Sea	ND–1200	(Gatidou et al. 2005)
	2005	USA	Puerto Rico US virgin Island	Harbor	ND–1300	(Carbery et al. 2006)
This exp.	2006–2009	Korea	The whole country	All kinds	ND–67.74	

High concentrations of chlorothalonil were detected in B1, B2, and B3 in Busan. Gamman Container Terminal, a representative port in Busan, is located in this region, and the high concentration was seen to be caused by the long-term anchoring of the larger ships. As for the Masan area, high concentrations of chlorothalonil were detected in M2, located inside the port, due to the influence of large ships and geological features (a rias coast).

The spatial distribution of pollution by the three antifouling agents in Korea has been investigated using the average value of the concentrations in 2006 and 2009 (Fig. 3). Chlorothalonil showed even distributions in all regions, except the eastern area of the Korean Peninsula. Particularly, the Ulsan and Incheon areas indicated high concentrations, presumably due to the influence of big harbors.

Like chlorothalonil, dichlofluanid also showed even distribution in all regions; in particular, Gunsan, Ulsan, and Masan indicated higher concentration distributions compared to other regions. Supposedly, these two substances' concentration distributions were even because of various sources of pollution, such as big harbors, the main source of pollution for antifouling agents, and the use of agricultural chemicals.

The pollution level of Irgarol 1051 tended to increase at big harbors in the southern coast, unlike the two aforementioned substances. This indicated the possibility that Irgarol 1051 is used solely as an antifouling agent in Korea, without serving any other functions, such as a herbicide. Particularly, Gunsan, Pusan, and Donghae Port showed high concentrations.

The comparison of this study and international studies is shown in Table 2. In Britain and Greece, ND–1.38 and ND–63 ng/L of chlorothalonil were detected, respectively. In this study, ND–67.96 ng/L was detected. The concentration in Korea was higher than in other countries except Greece, where it was similar.

Due to its quick degradation, the amount of dichlofluanid detected was below the detection limit, but large in a few regions. It was below the limit in the blackwater of Britain, the seawaters in Greece, and Italy. Since the results do not indicate unused dichlofluanid, more detailed research was conducted on dichlofluanid by studying the sediment and DMSA, a degradation product.

The concentration of dichlofluanid in the sediment of the blackwater of Britain was 668.2 ng/g, and 36 ng/L of DMSA was detected in Greece, indicating that the concentration of dichlofluanid was detected below the detection limit because of fast degradation in the seawater, not because of the small amount used (Voulvoulis et al. 2000; Hamwijk et al. 2005). In some regions, very high concentrations of dichlofluanid were detected; a maximum of 600 ng/L was detected in the seawater of Spain (Martinez et al. 2000). In this research, the concentration of dichlofluanid detected was ND–74.79 ng/L.

Since the use of TBT has been prohibited, there has not been any official discussion across the world regarding the regulation of use of new antifouling agents. However, Irgarol 1051 and Diruon are being regulated in Europe (Konstantinou 2006). The reason for the regulation is their low degradation rate and toxicity. The study by Callow and Willingham concluded that Irgarol 1051 does not have any

biodegradation under water, and the study by Okamure et al. reported that Irgarol 1051 only goes through photodegradation in water (Callow and Willingham 1996; Okamura et al. 1999).

Most study results reported the degradation process of Irgarol 1051 to be very slow, and many countries around the world are monitoring it continuously. In this research, the concentration of Irgarol 1051 was ND–67.74 ng/L, lower than ND–1,300 ng/L in America and ND–1,200 ng/L in Greece. Nonetheless, considering factors such as a half-life, it is deemed necessary to monitor continuously in Korea as well.

Conclusions

The study of three new antifouling agents at ten major bays in Korea in 2006 and 2009 indicated that the pollution level has increased in the coastal areas in Korea since 2006. Distribution of the pollution indicated that it is increasing in the western and southern regions. In particular, the pollution is increasing at big harbors in Ulsan, Busan, and Gunsan, with some areas possibly being affected by herbicides. Although the concentration in 2009 is higher than in 2006, the pollution level of Korea is similar or lower than those indicated in documents from foreign countries. However, as mentioned in the Results and Discussion, it is necessary to conduct a more detailed study on sediment and degradation products in order to further investigate the influence upon the marine ecosystem in the Korean coastal areas.

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