

Research Articles

Survey for the Occurrence of Antifouling Paint Booster Biocides in the Aquatic Environment of Greece

Vasilios A. Sakkas, Ioannis K. Konstantinou, Dimitra A. Lambropoulou and Triantafyllos A. Albanis*

Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

*Corresponding author (talbanis@cc.uoi.gr)

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Abstract. Since the restriction imposed by European Union regulations on the use of TBT-based antifouling paints on boats below 25 m in length, new terms have been introduced in the 'small boat' market. Replacement products are generally based on copper metal oxides and organic biocides. Several studies have demonstrated the presence of these biocides in European ports and marinas of Spain, France, Germany and the United Kingdom. An extended survey of the antifouling biocides chlorothalonil, dichlofluanid, irgarol 1051 and sea-nine 211 was carried out in Greek ports and marinas of high boating activities from October 1999 to September 2000. The sampling sites were: Piraeus, Elefsina, Thessaloniki, Patras, Chalkida, Igoumenitsa, and Preveza (Aktio). The extraction of these compounds from the seawater samples was performed off-line with C₁₈ solid phase extraction (SPE) disks while the determination was carried out with gas chromatography coupled to electron capture (ECD), thermionic (FTD) and mass spectroscopy (MS) detectors. The concentration levels of biocides were higher during the period from April to October. This seasonal impact depends on the application time of antifouling paints and mimic trends in the seasonal distribution of biocides in other European sites.

Keywords: Antifouling booster biocides; chlorothalonil; dichlofluanid; irgarol 1051; sea-nine 211

1 Introduction

For many years, tributyltin (TBT) compounds were the most widely used active ingredients in antifouling paints, but this has been regulated internationally since 1990 due to its severe impact on the aquatic ecosystem. The International Maritime Organization (IMO) and the Marine Environment Protection Committee (MEPC) have recently announced a proposed ban on the use of TBT as an antifouling agent (Champ 2000). This ban is likely to be introduced in 2003 and will lead to an increase in vessels using alternative 'TBT free' coatings containing copper combined with organic booster biocides. These coatings are already used and applied to the hulls of ships and boats to prevent the growth of bacteria, macroalgae, mussels and other invertebrates. Although nine booster biocides are approved in antifouling products (chlorothalonil, dichlofluanid, diuron, irgarol 1051, sea-nine 211, TCMS pyridine, TCMTB, zinc pyrithione and zineb) for amateur and professional use, only few data are

known about the environmental risks of antifouling coating systems containing such biocides (Ranke and Jastorff 2000, Thomas et al. 2001).

Recently, a number of studies in coastal waters indicated irgarol 1051 occurrence in the aquatic environment (Sargent et al. 2000, Tolosa et al. 1996, Gough et al. 1994). Diuron is another biocide that has been detected in significant levels in areas of high boating activity (Thomas et al. 2000, Ferrer and Barcelo 1999, Boxall et al. 2000) as well as dichlofluanid, chlorothalonil (Voulvounis et al. 2000), zinc pyrithione (Boxall et al. 2000) and sea-nine 211 (Martinez et al. 2000).

While large quantities of antifoulants enter the aquatic environment annually, there is little information on their partitioning behavior. Besides the accumulation of biocides in marine sediments their sorption behavior, if introduced as paint particles, is dictated by a number of physicochemical parameters in the aquatic environment. Factorial experiment performed subsequently with the application of a Mackay fugacity model (Voulvoulis et al. 2002) demonstrated that there is evidence of the influence of total organic carbon on the sorptive behavior of the biocides, although further experiments are needed to investigate its relationship to the binding mechanism of antifouling biocides in the natural environment. Sorption appeared to be enhanced by increased suspended matter, while salinity does not seem to play a significant role. The influence of pH is not clear.

Therefore, there is a requirement for information about the potential pollution problem posed by antifouling paints that contain booster biocides and that are used on leisure craft in Greek coastal waters. The aim of this work is to provide information, for the first time, on the presence of the biocides chlorothalonil, dichlofluanid, irgarol 1051 and sea-nine 211 in the Greek marine environment. For this purpose, an extended survey was conducted for a period of one year (October 1999 to September 2000) at eleven selected sampling sites (including ports and marinas) considering their special location in the Mediterranean Sea, as well as their particular environmental interest, since certain areas protected by the Ramsar Treaty are included.

Several analytical methods for the analysis of antifouling biocides in environmental waters have been developed and a full review of these methods has recently been undertaken (Voulvounis et al. 1999). In this study, an efficient multiresi-

due analytical method was developed for the determination of the target compounds at ng/L levels. The isolation of biocides from the water samples was carried out by means of solid-phase extraction (SPE), using C_{18} extraction disks. The qualitative and quantitative determination of the target compound was performed by gas chromatography coupled to mass spectroscopy (MSD), electron capture (ECD) and flame thermionic detectors (FTD).

2 Methods and Materials

2.1 Study area

Three of the busiest commercial ports and eight of the most popular marinas with high yachting activity around Greece have been selected as a study area to investigate the environmental occurrence of the antifouling paint booster biocides in subsurface waters. The ports were at the cities of Piraeus, Thessaloniki and Patras. The main marinas selected were two from Piraeus, and one each in the cities of Patras, Chalkida, Thessaloniki (Kalamaria), Preveza (Aktio), Elefsina and Igoumenitsa. Fig.1 shows the location of the sampling stations as well as some characteristic data. Piraeus is Greece's largest port located in the southwestern Aegean Sea (Saronikos Gulf). There are two main marinas adjacent to the Central Port, the Mikrolimano marina and the Pusalimani marina that can accommodate more than 800 vessels. The port of Thessaloniki is located in the northwest Aegean Sea on the northern shore of the Gulf of Thessaloniki (Thermaikos Gulf). The port of Thessaloniki is rapidly being developed to accommodate international cruise liners and local ferries as an outlet to the islands of the Aegean. The marina of Thessaloniki is in Kalamaria and it can accommodate approximately 250 boats from 5 to 30 meters long. Patra is located in the northwest of the Peloponnese region (Korinthiakos Gulf) and its port is a major transportation center linking Greece with Italy and the Peloponnese with the Ionian islands.



Fig. 1: Locations of the selected sites – characteristic data (Number of vessels, 1 ship = 50 vessels, Water exchange: (++) high, (+) medium, (–) low)

There is a closed marina near the port accommodating about 100 vessels throughout the year. Chalkida is the capital of Evia the second largest island of Greece. There is a closed marina near the city that can handle fewer than 60 vessels. Aktio marina is located in the entrance of Amvrakikos Gulf (Ionian Sea) that is one of the most important wetlands in Greece and is being protected by the Ramsar Treaty. It is capable of offering yacht repair and maintenance for more than 300 boats ashore. Greece's second biggest developed shipyard is in Elefsina located in 30 km north to Athens. The Elefsina shipyard concentrates on building ships for the Navy and repairing an average of 160 ships a year. There is a small marina close to the ship-repair zone which handles about 40 to 50 boats throughout the year. Igoumenitsa is the capital city of Thesprotia, located in the western part of Greece. Igoumenitsa is an important center of communication due to the fact that the port is the most northern one of western Greece and that it connects Greece with Italy and the rest of Europe. There is a marina near the port, which accommodates fewer than 100 leisure craft throughout the year.

2.2 Sampling

Water samples from the above ports and marinas were collected between the period of October 1999 to September 2000 (7–10 samplings) on a monthly basis during the high boating activity season (June–August 2000). The sampling was carried out at a depth of 1 m from the surface layer of the seawater and three different samples were collected each time that sampling from a station was conducted, in order to give a representative average of the concentration of the biocides. The samples were collected in 2.5-L precleaned amber glass bottles sealed with screw caps lined with aluminum foil. Samples, which reached the laboratory one day after sampling, were stored at 4°C, combined into one sample and extracted normally within 24 h.

2.3 Chemicals

Biocide standards, chlorothalonil (2,4,5,6-tetrachloro isophthalonitril), dichlofluanid (N^2 -dimethyl- N -phenyl sulphamide) and irgarol 1051 (2-methylthio-4-tertiary-butylamino-6-cyclopropylamino-s-triazine), were purchased from Riedel-de Häen (Germany). Sea-nine 211 (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one) was a gift from Rohm & Haas (Philadelphia, PA, USA). Pesticide grade n-hexane, methanol, dichloromethane and ethylacetate were purchased from Pestiscan (Labscan Ltd., Dublin, Ireland). Sodium sulfate (pro-analysis) and sulfuric acid was from Merck (Darmstadt, Germany). C_{18} extraction disks were purchased from Empore (St. Paul, USA) and a conventional filtration apparatus was purchased from Supelco (Bellefonte, USA).

2.4 Analytical techniques

Solid Phase Extraction (SPE) and chromatographic techniques were applied to quantify the biocides. The collected samples were adjusted to pH <3 with 1:1 (v/v) sulfuric acid. Methanol modifier (2.5 mL) was added to 500 mL water samples to

allow better extraction. C18 Empore extraction disks were conditioned with 10 mL of acetone for 2h. The disks were placed in the conventional filtration apparatus and washed with 5 mL of solvent mixture, dichloromethane: ethyl acetate (1:1, v/v) under vacuum, and with 5 mL of methanol for 3 min, with no vacuum applied. The disks were not allowed to become dry and the samples were allowed to percolate through the disks under vacuum. The compounds trapped in the disks were collected by using 2 x 5 mL of solvent mixture dichloromethane:ethyl acetate (1:1, v/v) as an eluting system. The extract was evaporated to a final volume of 0.1 mL in a gentle stream of nitrogen prior to GC analysis.

2.5 Gas chromatographic conditions

2.5.1 GC-ECD, GC-FTD

The analysis of chlorothalonil, dichlofluanid and sea-nine 211 was performed using a Shimadzu 14A capillary gas chromatograph equipped with ^{63}Ni electron capture detector (ECD) at 300°C and a dimethylpolysiloxane (DB-1) column, 30 m x 0.32 mm x 0.25 μm . The analysis of irgarol 1051, as well as the confirmatory analysis of chlorothalonil, dichlofluanid and sea-nine 211, was performed using a Shimadzu 14A capillary gas chromatograph equipped with flame thermionic detector (FTD) at 250°C and with a (5% Phenyl)-methylpolysiloxane column, 30 m x 0.32 mm x 0.25 μm . The temperature program used for the analysis of both columns was: from 55°C (2 min) to 210°C (15 min) at 5°C/min and to 270°C at 10°C/min. The injector temperature was set to 220°C in the splitless mode. For the GC-ECD system, helium and nitrogen were used as carrier and make-up gases, respectively. Helium was used as the carrier gas for the GC-FTD system. The detector gases were hydrogen and air, and the ion source of FTD was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire.

2.5.2 GC-MS

Confirmation of compounds was performed by GC-MS, using a QP 5000 Shimadzu instrument equipped with a DB-5-MS capillary column, 30 x 0.25 mm x 0.25 μm , containing (5% Phenyl)-methylpolysiloxane (J & W Scientific, Folsom, CA, USA) under the following chromatographic conditions: Injector temperature 220°C, oven temperature program 55°C (2 min) to 210°C (20 min) at 5°C/min and to 270°C at 10°C/min.

Helium was used as the carrier gas. The interface was kept at 290°C and the spectra were obtained at 70 eV. The splitless mode was used for injection. The analyses of the compounds were performed in the selected ion monitoring (SIM) mode. In this way, it was possible to establish the best conditions with respect to sensitivity and selectivity. The low biocide levels in seawater made the use of the SIM mode necessary, which provided response factors up to 10 times higher than the full scan mode. The ions (m/z) that were selected in order to quantify the response under the SIM mode were: 264, 266, 268 and 229 for chlorothalonil, 123, 167 and 224 for dichlofluanid, 182, 238 and 253 for irgarol 1051, and 169, 182 and 246 for sea-nine 211.

2.6 Quantification

Quantification was performed by external and internal calibration using authentic standards. The concentrations reported are mean values of duplicate or triplicate analysis, and relative standard deviations (R.S.D.s) of less than 13% were generally achieved. Recoveries of spiked biocides (0.05 $\mu\text{g/L}$ to 5 $\mu\text{g/L}$) in uncontaminated seawater and limits of determination using ECD, FTD and MS-SIM detectors are shown in Table 1. Appropriate corrections were made for recoveries.

3 Results and Discussion

The concentration levels of the biocides detected were higher during the high boating activity than during the remaining period of monitoring, especially in marinas revealing leaching ability and occurrence in the aquatic environment. A summary of the mean and the range of concentration levels detected is shown in Table 2.

3.1 Irgarol 1051

Irgarol 1051 was the most frequently detected biocide in this study. Highest concentrations of irgarol 1051 (ranged from 11 to 90 ng/L) are shown to be associated with yacht marinas which primarily house pleasure crafts. The mean detected concentrations ranged from 10 to 41 ng/L and the higher values were found in the Piraeus Mikrolimano marina (m1), which is the busiest enclosed marina of Piraeus. Direct contamination from the shipyard with irgarol 1051 due to ship painting, in addition to the normal leaching rate, cannot be excluded for the case of Elefsina marina where the mean concentration value was also high (31 ng/L).

Table 1: Recoveries of biocides spiked in seawater, and LODs in GC-ECD, GC-FTD and GC-MS(SIM) systems

Biocide	Recovery (%)		LOD ^a -RSD ^b					
	GC-ECD	GC-FTD	GC-MS		GC-ECD		GC-FTD	
			(ng/L)	(%)	(ng/L)	(%)	(ng/L)	(%)
Chlorothalonil	93±9	–	0.42	10	5.2	8	–	–
Dichlofluanid	56±13	–	1.0	9	9.5	9	–	–
Irgarol 1051	–	92±8	0.54	9	–	–	2.2	8
Sea-nine 211	84±10	–	0.64	11	6.3	9	–	–

^a Limit of determination for the whole analytical procedure

^b Relative standard deviation (mean of three replicate experiments, n=3)

Table 2: Summary of biocide concentrations detected from 11 sampling stations, ports (p) and marinas (m) during October 1999 to September 2000

Biocides	Mean Detected	Concentration (ng/L)		Detection ^a (%)
		Range		
Chlorothalonil^b				
Aktio (m)	N ^c =8	23	bdl ^d -55	75
Chalkida (m)	N=10	33	bdl-38	80
Elefsina (m)	N=7	37	bdl-63	71
Igoumenitsa (m)	N=8	15	bdl-29	75
Patra (m)	N=8	23	bdl-42	88
Patra (p)	N=8	22	bdl-26	50
Piraeus (m1) ^e	N=8	19	bdl-21	75
Piraeus (m2) ^f	N=8	16	bdl-19	38
Piraeus (p)	N=8	12	bdl-13	38
Thessaloniki (m)	N=10	13	bdl-17	80
Thessaloniki (p)	N=10	19	bdl-31	80
Dichlofluamid^b				
Aktio (m)		53	bdl-112	63
Chalkida (m)		186	bdl-284	80
Elefsina (m)		102	bdl-214	86
Igoumenitsa (m)		36	bdl-52	50
Patra (m)		148	90–222	100
Patra (p)		72	bdl-88	75
Piraeus (m1)		61	bdl-88	50
Piraeus (m2)		58	bdl-162	75
Piraeus (p)		26	bdl-26	13
Thessaloniki (m)		63	bdl-68	60
Thessaloniki (p)		24	bdl-36	60
Irgarol 1051^g				
Aktio (m)		14	8–27	100
Chalkida (m)		nd ^h	nd	nd
Elefsina (m)		31	bdl-55	86
Igoumenitsa (m)		14	bdl-22	88
Patra (m)		19	12–24	100
Patra (p)		nd	nd	nd
Piraeus (m1)		41	15–90	100
Piraeus (m2)		29	11–76	100
Piraeus (p)		18	10–24	100
Thessaloniki (m)		10	bdl-11	60
Thessaloniki (p)		nd	nd	nd
Sea-Nine 211^b				
Patra (m)		49	bdl-49	12

^a Referring to: No. of samples detected/total no. of samples^b quantified by GC-ECD^c number of samplings^d below detection limit^e Piraeus Mikrolimano marina^f Piraeus Pasalimani marina^g quantified by GC-FTD^h not detected

The second busiest marina of Piraeus, Pasalimani marina (m2), also demonstrated constantly high values of irgarol 1051 with a mean concentration of 29 ng/L. Lowest concentrations were found at the remaining marinas, possibly due to a direct connection to the sea, resulting in a renewing of the surface water. In the case of Chalkida marina, although it has low water-exchange capabilities, irgarol 1051 was not detected at all, thus leading one to assume that this antifouling agent is not applied at this area. Ports, which generally have a lower density of pleasure craft, and more and larger vessels (commercial ships), are not shown to be contaminated by this biocide, with the exception of Piraeus port where concentration levels ranged from 10 to 24 ng/L. The concentrations found were much lower than those seen in other studies. A survey of marinas on Lake Geneva (Toth et al. 1996) showed concentrations less than 145 ng/L, while other studies showed significantly higher concentrations for this biocide (Readman et al. 1993, Biselli et al. 2000, Zhou et al. 1996). The aquatic behavior of irgarol 1051 is not well understood, although it is seen to be widely occurrent in marine waters around Europe as well as in other continents (Okamura et al. 2000). Generally, although the degradation of irgarol 1051 seems to be slow in seawater (Scarlett et al. 1997), several studies have reported biodegradation, photodegradation and hydrolysis of this compound leading to 2-methylthio-4-tert-butylamino-6-amino-s-triazine as the degradation byproduct (Ferrer and Barcelo 1999). Tolosa et al. (1996) and Ferrer et al. (1997) suggested that irgarol 1051 has a low affinity for particulate matter ($\log K_{oc}=3.0$, $\log K_{ow}=3.9$) and is associated with the dissolved phase in most marine waters. However, other studies have shown significant concentrations in sediments, implying that partition does occur (Thomas et al. 2000, Voulvounis et al. 2000).

3.2 Chlorothalonil

The existence of chlorothalonil was confirmed during the whole year of monitoring with higher concentrations found in the months of high boating activity. The major concentrations observed were 63 and 31 ng/L in the Elefsina marina and the Thessaloniki port, respectively. Elefsina marina, with a mean concentration of 37 ng/L, was the most contaminated marina, possibly due to the fact that it is close to the shipyard and direct contamination due to ship painting is easy to occur. Chalkida marina also demonstrated a high mean concentration (33 ng/L) due to being a very tightly closed marina with a low water renewing time. Lower concentrations were observed in other marinas maybe due to the daily wash out of the water from marinas to the open sea. Although Patra port had the highest mean concentration (22 ng/L), this was observed during May to September 2000. The same tendency was observed for the Piraeus port, but not in Thessaloniki port where the persistence of chlorothalonil was observed during the whole year, thus showing that an agricultural run-off effect cannot be excluded. No previous studies have reported coastal water contamination with chlorothalonil, except Voulvounis et al. (2000), but the concentrations observed seemed to also be related to agri-

cultural applications in the specific study area. The low concentrations detected are due to the generally low leaching potential as well as the lack of persistence of the biocide in the aquatic environment. As has been reported, chlorothalonil can undergo either biodegradation or photodegradation in the water column demonstrating a half-life of a few hours (Caux et al. 1996).

3.3 Dichlofluanid

Dichlofluanid has also been detected in the seawater samples, and in higher concentration levels than the other antifouling biocides, especially in the closed marinas in the months of the highest boating activity. The concentration levels for the marine sampling stations ranged from 24 to 284 ng/L with mean values ranging from 36 to 186 ng/L. The highest concentration was observed in the marina of Chalkida. Although this marina can accommodate less than 60 vessels, it is a very tightly closed marina with a low water renewing time, resulting in constantly high detectable concentrations of dichlofluanid. As far as the ports are concerned, the concentration levels ranged from 16 to 88 ng/L detected only in the months of April to September. Patra's port is the most contaminated with a mean concentration of 72 ng/L. The fact that the marina of Patra is also contaminated by constantly high values of dichlofluanid can lead to the assumption that this antifouling ingredient is the most widely used in paint formulations in this area. Elefsina marina has also high concentration values of this biocide, showing that its position close to shipyard is a very essential factor for contamination. High concentration levels of dichlofluanid in other marinas and ports is in agreement with our unofficial market survey showing that this paint is the most commonly used throughout Greece. The concentration levels detected are lower than in other studies observing the presence of dichlofluanid in Spanish ports and marinas (Martinez et al. 2000). Voulvounis et al. (2000) observed considerable concentrations of dichlofluanid in sediments in a commercial estuary in the UK, but the study performed by Thomas et al. (2000) showed negligible concentrations in marina water and sediments. Only little data is known about its occurrence in the aquatic environment, even though it has been widely used on various crops.

3.4 Sea-nine 211

It should be pointed out that sea nine 211 was detected in only one sampling station and at one time in the marina of Patras at a concentration of 49 ng/L when the activity of pleasure craft vessels was the highest (August 2000). This could be due to the fact that the biocide degrades rapidly. Sea-nine 211 was only detected in marinas of Catalonia (Martinez et al. 2000) in considerable concentrations, but for a period of only one month, which seems to be in agreement with our observation. Some information is available about this biocide, although, according to Jacombson and Willingham, (2000), sea-nine 211 is degraded both biologically and chemically in the environment, and it does not

bioaccumulate. The hydrolytic half-life of sea-nine 211 determined by this study was >720h for a pH 7 buffered solution, while degradation in natural seawater containing microorganisms showed a half-life of less than 24h. Photolysis experiments conducted at pH 7, were also rapid ($t_{1/2}=322$ h). The manufacturer's data comparisons show that the biocide partitions to sediment more strongly than TBT-based antifouling paints and its metabolites are 100.000 times less toxic than the parent compound. Sea-nine was rewarded with the 'Green Chemistry Challenge Award' from the U.S. EPA for its environmental safety as a marine antifouling agent.

Although the concentration levels of the antifouling booster biocides detected were not high enough to have acute toxic effects directly on higher species, their chronic effects at low concentrations are unknown and difficult to determine.

4 Conclusions

A 1-year survey (from October 1999 to September 2000) has been conducted to evaluate the presence of antifouling booster biocides in environmental seawater samples collected around Greece, concerning the major ports and marinas. The concentration levels of the biocides detected were not high enough for the aquatic environment, but they showed a seasonal dependence influenced by the boating density, which plays a dominant role. However, the use of the above compounds as additives in antifouling paints is going to be increased due to the complete ban on the use of TBT, so further studies have to be conducted concerning the occurrence and the fate of these booster biocides in the aquatic environment. It is essential that an official detailed record concerning the type and the quantities of the antifouling paints used by boat owners, and at the treatment sites, be kept by Greek authorities in order to estimate more clearly their persistence and occurrence in the aquatic environment.

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