

Chapter 3

Emerging Issues on Contamination and Adverse Effects by Alternative Antifouling Paints in the Marine Environments

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Abstract The current status of antifouling biocides contaminations was reviewed in water, sediment, and biological samples, and the effect of antifouling biocides for aquatic organisms was evaluated.

Irgarol 1051 (3-methylthio-4-tetrabutylamino-6-cyclopropylamino-*s*-triazine), diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), sea nine 211 (2-*n*-octyl-4,5-dichloro-2-methyl-4-isothiazolin-3-one), chlorothalonil (2,4,5,6-tetrachloro-isophthalonitrile), dichrofluanid (*N'*-dimethyl-*N*-phenylsulphamide), metal pyrithions (metal complex of 2-mercaptopyridine-1-oxide), and PTPB (pyridine triphenylborane) in water were in the range of 0.5–2,430 ng/l, <0.7–6,742 ng/l, <0.3–3,700 ng/l, <1–1,380 ng/l, <1–55 ng/l, <80 ng/l, and 0.0036–0.021 ng/l, respectively. The concentrations of Irgarol 1051, diuron, sea nine 211, chlorothalonil, dichrofluanid, and pythiones in sediment were in the range of <0.02–816 µg/kg dry, <0.02–1,350 µg/kg dry, <0.04–150 µg/kg dry, <0.01–46.5 µg/kg dry, <0.1–688.2 µg/kg dry, <8–420 µg/kg dry, respectively. Irgarol 1051 was detected in the range of <0.1–35 µg/kg in clam, mussel, and oyster from Vietnam, Thailand, and Japan. The concentrations of diuron and sea nine 211 in bivalves were <0.1–9.6 µg/kg and <0.1–0.3 µg/kg, respectively.

EC₅₀ and LC₅₀ of Irgarol 1051 were in the range of 0.09–50,800 µg/l and 0.38 to >40,000 µg/l, respectively. EC₅₀ of sea nine 211 were in the range of 0.42–12 µg/l. EC₅₀ and LC₅₀ of diuron were in the range of 4.3–43,000 µg/l and 5.9 to >127,000 µg/l, respectively. EC₅₀ and LC₅₀ of chlorothalonil were in the range of 4.4–390 µg/l and 12–110 µg/l, respectively. EC₅₀ of dichlofluanid was in the range of 87–1,050 µg/l. EC₅₀ of tolylfluanid was in the range of 9.9–405 µg/l. EC₅₀ and LC₅₀ of PTPB were in the range of 2.2–140 µg/l and 54 µg/l, respectively.

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EC₅₀ of TCMTB ((2-thiocyanomethylthio) benzothiazole) was in the range of 46–433 µg/l.

Judging from toxicity data, most of these alternative biocides concentrations which were detected in the aquatic environment were below the level that causes an adverse effect in aquatic organisms.

Keywords Alternative biocide • Water • Sediment • Biota • Concentration • Toxicity

3.1 Introduction

Organotin (OT) compounds leaching from antifouling paints have caused many deleterious effects, including imposex and abnormal shell morphology, on nontarget aquatic organisms (Gibbs et al. 1988; Waldock and Thain 1983). As a result, OTs have led to a decrease in aquatic products (Bryan et al. 1986). OT application to large vessels has been banned or restricted in some countries since the 1980s. Even after the enforcement of the regulation, OTs have been detected at higher concentrations in water, sediment, and biota from harbours, marinas, and estuaries, particularly where boat activity is high and the water flushes poorly (Harino et al. 1998a, b). Furthermore, comparatively high concentrations of butyitin and phenyltin compounds have been detected in sediments, mussels, fish, and marine mammals (Tanabe et al. 1998; Harino et al. 1999, 2002, 2003, 2007a; Midorikawa et al. 2004). In October 2001, the International Maritime Organization (IMO) adopted the International Convention on the Control of Harmful Antifouling Systems (AFS Convention), which prohibited the use of OTs as active ingredients in antifouling systems for ships. Following the international restrictions on the use of OT-based antifoulants, paint manufacturers have developed many products as alternatives to the use of OTs. More than 20 chemical substances have been used or proposed as alternative compounds. When these antifouling biocides from the hulls of ships, fishing nets, etc. are released into the aquatic environment, these chemicals are distributed to water, sediment, and aquatic organisms. Therefore, it is important to identify the level of the antifouling biocides in the aquatic environment. Furthermore, the effects of alternative biocides on aquatic organisms are of concern, because most alternative biocides have been used as pesticides.

The research on contamination of alternative compounds in the aquatic environment started in early 1990. Since then many papers have been published. The distributions of representative antifouling biocides such as Irgarol 1051 (3-methylthio-4-tetrabutylamino-6-cyclopropylamino-*s*-triazine), diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), sea nine 211 (2-*n*-octyl-4,5-dichloro-2-methyl-4-isothiazolin-3-one), chlorothalonil (2,4,5,6-tetrachloro-isophthalonitrile), dichlofluanid (*N'*-dimethyl-*N*-phenylsulphamide), zinc pyrithiones (zinc complex of 2-mercaptopyridine-1-oxide), copper pyrithiones (copper complex of 2-mercaptopyridine-1-oxide), and PTPB (pyridine triphenylborane)

in water, sediment, and biological samples and the effects of antifouling biocides on aquatic organisms are reviewed in this chapter.

3.2 Occurrences of Antifouling Biocide

3.2.1 Concentration in Aquatic Environment

There are many papers concerning the concentrations of Irgarol 1051. The concentrations of Irgarol 1051, which were reported between 1993 and 2012, are shown in Table 3.1. The presence of Irgarol 1051 in the surface waters of marinas on the Cote d'Azur, Monaco, was first reported at concentrations of up to 1,700 ng/l in 1993 by Readman et al. (1993). Since then, the occurrence of Irgarol 1051 has been reported in various European countries. The concentrations of Irgarol 1051 in coastal waters of England, German, Greece, Spain, Monaco, and Bermuda showed ranges of <0.5–1,424, 2.2–900, 11–440, 3–665, 5–1,700, and 10–590 ng/l, respectively (Readman et al. 1993; Gough et al. 1994; Toth et al. 1996; Tolosa et al. 1996; Connelly et al. 2001; Scarlett et al. 1999; Biselli et al. 2000; Ferrer and Barcelo 2001; Thomas et al. 2001, 2002; Boxall et al. 2000; Voulvoulis et al. 2000; Sargent et al. 2000; Sakkas et al. 2002; Martinez et al. 2001; Bowman et al. 2003; Lambert et al. 2006; Zhou 2008). Irgarol 1051 was detected in the range of 1–254 ng/l in water from the USA (Sapozhnikova et al. 2013). It was reported that Irgarol 1051 was also detected in Asian countries. The concentrations of Irgarol 1051 in Japan, Korea, and Malaysia were ranged <0.8–267, <1–14, and <1–2,012 ng/l, respectively (Okamura et al. 2000a; Harino et al. 2004; Eguchi et al. 2010; Liu et al. 1999; Ali et al. 2013). These levels found in the estuary may cause photosynthetic inhibition for nontarget algae (Sargent et al. 2000). GS26575 (2-methylthio-4-tert-butylamino-6-amino-*s*-triazine) was detected in the area where Irgarol 1051 was detected. Okamura et al. (2000a) reported that the maximum concentration of GC26575 was 1,870 ng/l in the Seto Inland Sea of Japan (Tables 3.1 and 3.2).

The concentrations of diuron and its degradation compounds are shown in Table 3.2. Several studies have measured diuron in the coastal waters of England. The concentrations of diuron in water varied in each area, and its maximum concentration was 6,742 ng/l in Crouch Estuary, England (Thomas et al. 2001). The levels of diuron reported in England, Spain, Japan, USA, and Korea were in the range of <1–6,742, 2–1,030, <0.7–1,540, 2–68, and 35–1,360 ng/l, respectively. Concentrations of diuron reported in these countries were similar levels to those in England.

As the degradation products of diuron, DCPMU (1-(3,4-dichlorophenyl)-3-methylurea), DCPU (1-(3,4-dichlorophenyl)urea), and CPMU (1-(3-chlorophenyl)-3,1-dimethylurea) were confirmed to have been produced in the aquatic environment, and the concentrations of DCPMU, DCPU and CPMU were in the range of <1–78, <1–6, and <1–5 ng/l, respectively (Thomas et al. 2002). Thomas et al. (2002) reported

Table 3.1 Concentrations of Irgarol 1051 and its degradation compounds in water samples (means in parentheses)

Chemical	Location	Year	Concentrations (ng/l)	References
Irgarol 1051	Mediterranean Sea (Cote d'Azur), Monaco	1993	5–1,700	Readman et al. (1993)
	Medway estuary, England	1993	4–18 (11)	Gough et al. (1994)
	Humble estuary, England	1993	12–190 (84)	Gough et al. (1994)
	The Solent and English Channel, England	1993	2–11	Gough et al. (1994)
	Lake Geneva, Switzerland	1994–1995	2.5–145	Toth et al. (1996)
	Mediterranean Sea (Cote d'Azur), Monaco	1995	1.5–640	Tolosa et al. (1996)
	Hamilton Harbour, Bermuda, England	1995	10–590 (112)	Connelly et al. (2001)
	Seto Inland Sea, Japan	1996–1997	<5–264 (19)	Liu et al. (1999a)
	Plymouth Sound, England	1997	<1–127 (40)	Scarlett et al. (1999)
	North Sea, Germany	1997	11–170 (51)	Bissilli et al. (2000)
	Baltic Sea, Germany	1997	60–440 (266)	Bissilli et al. (2000)
	Masnou marina, Spain	1997–1998	3–119 (37)	Ferrer and Barcelo (2001)
	Crouch estuary, England (yachting season)	1998	<1–49 (9.2)	Thomas et al. (2001)
	Crouch estuary, England (off season)	1998	<1–9.4 (8.4)	Thomas et al. (2001)
	Southampton, England (yachting season)	1998	<1–141 (23)	Thomas et al. (2001)
	Southampton, England (off season)	1998	<1–1,421 (405)	Thomas et al. (2001)
	Sutton Harbour, England (yachting season)	1998	<1–84 (8.5)	Thomas et al. (2001)
	Sutton Harbour, England (off season)	1998	11–80 (54)	Thomas et al. (2001)
	Seto Inland Sea, Japan	1998	<5–142 (29)	Okamura et al. (2000a)
	Hamble estuary, England	1998–1999	(25)	Boxall et al. (2000)
Owell estuary, England	1998–1999	(48)	Boxall et al. (2000)	
Blackwater estuary, England	1998–1999	<50–680 (148)	Voulvoulis et al. (2000)	
Corwy marina, England	1999	7–543 (126)	Sargent et al. (2000)	
Coastal area, Greece	1999–2000	2.2–900 (16)	Sakkas et al. (2002)	

(continued)

Table 3.1 (continued)

Chemical	Location	Year	Concentrations (ng/l)	References
	Mediterranean Sea, Spain	1999–2000	20–665	Martinez et al. (2001)
	Florida (Biscayne Bay), USA	1999–2000	<1–60.9 (5.2)	Gardinali et al. (2002)
	Brighton marina, England	1999–2001	<1–964 (32)	Bowman et al. (2003)
	Southampton, England	2000	<1–305 (36)	Thomas et al. (2002)
	River, East Anglia, UK	2001	1–1,310 (259)	Lambert et al. (2006)
	Broads, East Anglia, UK	2001	12–2,430 (430)	Lambert et al. (2006)
	Broads, East Anglia, UK	2001	3–231 (48)	Lambert et al. (2006)
	The Port of Osaka, Japan	2002–2003	<0.8–267 (13)	Harino et al. (2004)
	Southern England	2004–2005	<3.1–89 (10)	Zhou (2008)
	Maizuru Bay, Japan	2007	2–18 (7)	Harino et al. (2010)
	California, USA	2008	2–254 (67)	Sapozhnikova et al. (2013)
	Jinhae Bay, Korea	2009	<0.1–14 (2.6)	Kim et al. (2014)
	Peninsular Malaysia, Malaysia	2011–2012	<1–2,012 (186)	Ali et al. (2013)
GS26575	Seto Inland Sea, Japan	1997–1998	<1–1,870 (15)	Okamura et al. (2000a)
	Masnou marina, Spain	1997–1998	4–23 (10)	Ferrer and Barcelo (2001)
	Southampton, England	2000	<1–59 (8)	Thomas et al. (2002)
	River, East Anglia, UK	2001	1–139 (16)	Lambert et al. (2006)
	Southern England	2004–2005	<0.5–30 (5.5)	Zhou (2008)
	Maizuru Bay, Japan	2007	<1.9	Harino et al. (2010)
	California, USA	2008	1–62 (18)	Sapozhnikova et al. (2013)

that the concentrations of DCPMU were high, because DCPMU is the primary degradation product of diuron in aerobic conditions.

There are many papers concerning the concentrations of sea nine 211 in water (Table 3.3). Sea nine 211 was not detected in water from marinas on the south coast of the UK and Maizuru Bay, Japan (Thomas et al. 2002; Eguchi et al. 2010).

Table 3.2 Concentrations of diuron and its degradation compounds in water samples

Chemical	Location	Year	Concentrations (ng/l)	References
Diuron	Crouch estuary, England (yachting season)	1998	<5–305 (36)	Thomas et al. (2001)
	Crouch estuary, England (off season)	1998	0.6–117 (22)	Thomas et al. (2001)
	Southampton, England (yachting season)	1998	1–33 (2265)	Thomas et al. (2001)
	Southampton, England (off season)	1998	<1–101 (8.3)	Thomas et al. (2001)
	Sutton Harbour, England (yachting season)	1998	<1–6,742 (90)	Thomas et al. (2001)
	Sutton Harbour, England (off season)	1998	<1–8.7 (14)	Thomas et al. (2001)
	Hamble estuary, England	1998–1999	(123)	Boxall et al. (2000)
	Owall estuary, England	1998–1999	(208)	Boxall et al. (2000)
	Mediterranean Sea, Spain	1999–2000	2–1,030	Martinez et al. (2001)
	Southampton, England	2000	16–1,249 (310)	Thomas et al. (2002)
	River, East Anglia, UK	2001	8–1,169 (58)	Lambert et al. (2006)
	Broads, East Anglia, UK	2001	65–249 (112)	Lambert et al. (2006)
	The Port of Osaka, Japan	2002–2003	<0.7–1,540 (126)	Harino et al. (2004)
	Maizuru Bay, Japan	2007	0.01–0.26 (0.08)	Eguchi et al. (2010)
California, USA	2008	2–68 (6)	Sapozhnikova et al. (2013)	
Jinhae Bay, Korea	2009	35–1,360 (172)	Kim et al. (2014)	
DCPMU	Southampton, England	2000	<1–78 (19)	Thomas et al. (2002)
DCPU	Southampton, England	2000	<1–6 (<1)	Thomas et al. (2002)
CPMU	Southampton, England	2000	<1–5 (<1)	Thomas et al. (2002)

Martinez et al. (2001) reported that sea nine 211 was detected in water from the Mediterranean Sea of Spain in the range of 2,600–3,700 ng/l. Furthermore, sea nine 211 in coastal water of Greece and Japan was detected in the range of 6.3–49 and <1–4 ng/l, respectively (Sakkas et al. 2002; Harino et al. 2004).

There are a few papers concerning chlorothalonil, dichlofluanid pyriothions, and PTPB (Table 3.3). Chlorothalonil was not detected in water from Southampton,

Table 3.3 Concentrations of the other alternative biocides in water samples

Chemical	Location	Year	Concentrations (ng/l)	References
Sea nine 211	Mediterranean Sea, Spain	1999–2000	2,600–3,700	Martinez et al. (2001)
	Coastal area, Greece	1999–2000	6.3–49	Sakkas et al. (2002)
	Southampton, England	2000	<1	Thomas et al. (2002)
	The Port of Osaka, Japan	2002–2003	<0.3–4 (2)	Harino et al. (2004)
	Maizuru Bay, Japan	2007	<1	Harino et al. (2010)
Chlorothalonil	Blackwater estuary, England	1998–1999	<200–1,380 (252)	Voulvoulis et al. (2000)
	Southampton, England	2000	<1	Thomas et al. (2002)
Dichlofluanid	Blackwater estuary, England	1998–1999	<24	Voulvoulis et al. (2000)
	Coastal area, Greece	1999–2000	5.2–55 (21)	Sakkas et al. (2002)
	Mediterranean sea, Spain	1999–2000	<20	Martinez et al. (2001)
	Southampton, England	2000	<1	Thomas et al. (2002)
Pyrithion	Maizuru Bay, Japan	2007	<80	Harino et al. (2010)
PTPB (pyridine triphenylborane)	Hiroshima Bay, Japan	2011	0.0048–0.021 (0.01)	Mochida et al. (2012)

England and the Mediterranean Sea, Spain. However, the average concentration of chlorothalonil from Blackwater Estuary, England, was 252 ng/l (Voulvoulis et al. 2000). Dichlofluanid was not detected in water samples from most coastal areas. However, dichlofluanid was detected at 52–55 ng/l in the coastal waters of Greece (Sakkas et al. 2002). Pyrithion (zinc pyrithion and copper pyrithion) were not detected in water samples of Maizuru Bay, Japan (Harino et al. 2010). PTPB, however, was detected in water in the range 4.8–21 pg/l (Mochida et al. 2012).

The concentrations of Irgarol 1051 in sediment are summarized in Table 3.4. Irgarol 1051 was detected in the range of <0.1–45 µg/kg dry in England (Thomas et al. 2002; Zhou 2008). In sediment from ASEAN countries, Irgarol 1051 was detected as 0.05–4.0 µg/kg dry, <0.1–4.9 µg/kg dry, and <0.02–14 µg/kg dry for Vietnam, Thailand, and Malaysia, respectively (Harino et al. 2004, 2007b, 2009b). The concentrations of Irgarol 1051 in sediment of the Port of Osaka, Otsuchi Bay, and Maizuru Bay, Japan were 7–816, <0.05–100, and <0.08–9.8 µg/kg dry, respectively (Harino et al. 2004, 2007b; Eguchi et al. 2010). Irgarol 1051 was

Table 3.4 Concentrations of Irgarol 1051 and GS26575 in sediment samples

Chemical	Location	Year	Concentrations ($\mu\text{g}/\text{kg}$ dry)	References
Irgarol 1051	Southampton, England	2000	<0.1–0.3 (0.2)	Thomas et al. (2002)
	Southampton, England	2000	0.3–3.5 (0.8)	Thomas et al. (2002)
	Coastal area, Vietnam	2002	0.05–4.0	Harino et al. (2006a)
	The Port of Osaka, Japan	2002–2003	7–816 (641)	Harino et al. (2004)
	Gulf of Thailand, Thailand	2004	<0.1–4.9 (0.62)	Harino et al. (2006b)
	Southern England	2004–2005	<1.7–45 (16)	Zhou (2008)
	Otsuchi Bay, Japan	2005	<0.05–100 (4.7)	Harino et al. (2007b)
	Nankai Trough, Japan	2006	<0.1–0.2 (0.08)	Harino et al. (2009a)
	Peninsular Malaysia, Malaysia	2006	<0.02–14 (1.7)	Harino et al. (2009b)
	Melaka, Malaysia	2006	<0.02–0.21 (0.09)	Harino et al. (2009b)
	Johor, Malaysia	2006	<0.02–0.9 (0.25)	Harino et al. (2009b)
	Suruga Bay, Japan	2006–2007	0.1 (0.1)	Harino et al. (2009a)
	Tosa Bay, Japan	2007	<0.1–0.2 (0.08)	Harino et al. (2009a)
	Maizuru Bay, Japan	2007	<0.08–9.8 (3.9)	Harino et al. (2010)
GS26575	Coastal area, Vietnam	2002	<0.1–0.43	Harino et al. (2006a)
	Gulf of Thailand, Thailand	2004	0.03–3.2 (0.50)	Harino et al. (2007a)
	Southern England	2004–2005	<0.9–14 (4.3)	Zhou (2008)
	Otsuchi Bay, Japan	2005	<0.18–0.47 (0.04)	Harino et al. (2007b)
	Peninsular Malaysia, Malaysia	2006	<0.09	Harino et al. (2009b)
	Melaka, Malaysia	2006	<0.09–0.49 (0.04)	Harino et al. (2009b)
	Johor, Malaysia	2006	<0.09	Harino et al. (2009b)
	Maizuru Bay, Japan	2007	<0.18	Harino et al. (2010)

also detected even in sediment collected in the deep sea (water depth, 4000 m) of Nankai Trough, Suruga Bay, and Tosa Bay, Japan, although the concentrations were in the range of $<0.1\text{--}0.2\ \mu\text{g}/\text{kg}$ dry, which were lower than those detected in the coastal areas (Harino et al. 2009a).

The concentrations of diuron in sediment are shown in Table 3.5. Diuron was detected in various areas of England at concentrations in the range of $<0.31\text{--}3,500\ \mu\text{g}/\text{kg}$ dry (Gough et al. 1994; Thomas et al. 2000, 2002; Boxall et al. 2000; Voulvoulis et al. 2000). Furthermore, diuron was detected in sediments of Switzerland and Germany in the range of $<0.2\text{--}8$ and $3\text{--}220\ \mu\text{g}/\text{kg}$ dry, respectively (Toth et al. 1996; Biselli et al. 2000). The concentrations of diuron in ASEAN countries such as Vietnam, Thailand, and Malaysia were $<0.02\text{--}9.9\ \mu\text{g}/\text{kg}$ dry (Harino et al. 2004, 2006, 2009b). Diuron was also detected in sediment of the coastal area and deep sea such as Nankai Trough, Suruga Bay, and Tosa Bay, Japan with concentrations of $<0.2\text{--}1,350\ \mu\text{g}/\text{kg}$ dry and $<0.02\text{--}12\ \mu\text{g}/\text{kg}$ dry, respectively (Harino et al. 2004, 2009a). The degradation product of diuron was not detected in sediment from England (Thomas et al. 2002).

The concentrations of sea nine 211 detected in sediment are summarized in Table 3.6. Harino et al. (2004) reported that concentrations of sea nine 211 in sediment from Japan ranged $0.04\text{--}150\ \mu\text{g}/\text{kg}$ dry. It was reported that sea nine 211 was detected in sediment of ASEAN countries in the range of $<0.02\text{--}4.2\ \mu\text{g}/\text{kg}$ dry (Harino et al. 2006a, b; 2009b).

Chlorothalonil is known to have been detected in sediments of England at concentrations of $<0.1\text{--}688\ \mu\text{g}/\text{kg}$ dry (Voulvoulis et al. 2000; Thomas et al. 2002). On the other hand, no detection of dichlofluanid in sediment has been reported. Pyrithions were detected in sediment from Vietnam and Japan at concentrations of $422\ \mu\text{g}/\text{kg}$ dry and $22\ \mu\text{g}/\text{kg}$ dry, respectively (Harino et al. 2006a, 2007b).

There are only a few papers concerning the detection of alternative biocides in biological samples in benthic animals (Table 3.7). Irgarol 1051 was detected in the range of $<0.1\text{--}35\ \mu\text{g}/\text{kg}$ in benthos such as clam, mussels and oysters from Vietnam, Thailand, and Japan (Harino et al. 2006a, b, 2007b, 2010). The concentrations of diuron and sea nine 211 detected in biota were $0.1\text{--}9.6\ \mu\text{g}/\text{kg}$ and $<0.1\text{--}0.3\ \mu\text{g}/\text{kg}$, respectively.

3.2.2 Geological Distribution of Antifouling Biocides

Sargent et al. (2000) pointed out that the concentrations of Irgarol 1051 in water were not influenced by salinity, pH, or temperature and that there was a strong positive correlation between average concentrations of Irgarol 1051 and the density of boating activity. Concentrations of Irgarol 1051 in the lock marina were high and its concentrations in the open marina were low (Boxall et al. 2000). The lock marina was directly adjacent to the slipway where paint particles from pressure-washing and paint scraping may have entered the marina. Higher concentrations of Irgarol

Table 3.5 Concentrations of diuron and its degradation compounds in sediment samples

Chemical	Location	Year	Concentrations ($\mu\text{g}/\text{kg}$ dry)	References
Diuron	Hamble estuary, England	1993	<10–132	Gough et al. (1994)
	Lake Geneva, Switzerland	1994–1995	<0.2–8	Toth et al. (1996)
	North Sea, Germany	1997	3–25 (12.5)	Bisslli et al. (2000)
	Baltic Sea, Germany	1997	4–220 (67.8)	Bisslli et al. (2000)
	Southampton, England	1998	<1–11 (8.2)	Thomas et al. (2000)
	Hamble estuary, England	1998–1999	6.3	Boxall et al. (2000)
	Orwell estuary, England	1998–1999	257	Boxall et al. (2000)
	Blackwater estuary, England	1998–1999	<0.31–222.3 (145)	Vouvoulis et al. (2000)
	Southampton, England	2000	0.4–6.2 (1.7)	Thomas et al. (2002)
	Southampton, England	2000	300–3,500 (880)	Thomas et al. (2002)
	Coastal area, Vietnam	2002	0.11–3.0	Harino et al. (2006a)
	The Port of Osaka, Japan	2002–2003	0.637–1,350 (39.4)	Harino et al. (2004)
	Gulf of Thailand, Thailand	2004	<0.08–5.7 (3.5)	Harino et al. (2006b)
	Otsuchi Bay, Japan	2005	0.06–530 (25.1)	Harino et al. (2007b)
	Nankai Trough, Japan	2006	<0.2–0.5 (0.2)	Harino et al. (2009a)
	Peninsular Malaysia, Malaysia	2006	<0.02–4.8 (0.84)	Harino et al. (2009b)
	Melaka, Malaysia	2006	<0.02–4.1 (0.51)	Harino et al. (2009b)
	Johor, Malaysia	2006	<0.02–9.9 (2.1)	Harino et al. (2009b)
	Suruga Bay, Japan	2006–2007	0.4–1.5 (0.95)	Harino et al. (2009a)
	Tosa Bay, Japan	2007	<0.2	Harino et al. (2009a)
Maizuru Bay, Japan	2007	<0.08–12 (5.4)	Harino et al. (2010)	

(continued)

Table 3.5 (continued)

Chemical	Location	Year	Concentrations ($\mu\text{g}/\text{kg}$ dry)	References
DCPMU (1-(3,4-dichlorophenyl)-3-methylurea)	Southampton, England	2000	<0.1	Thomas et al. (2002)
DCPU (1-(3,4-dichlorophenyl) urea)	Southampton, England	2000	<0.1	Thomas et al. (2002)
CPMU (1-(3-chlorophenyl)-3,1-dimethylurea)	Southampton, England	2000	<0.1	Thomas et al. (2002)

1051 were determined in areas of both high yachting activity such as mooring areas and the marina (Thomas et al. 2001). Diuron shows a similar geological distribution to Irgarol 1051 (Boxall et al. 2000; Thomas et al. 2001). Harino et al. (2004) reported that drastically higher concentrations of alternative biocides were observed at certain locations, where small- and medium-hull vessels were moored in poorly flushed zones. These papers imply that the concentrations of alternative biocides tend to be higher in areas of high shipping activity with poor flushing zones.

Interestingly, it is reported that in marinas of England, the concentration of diuron were higher than those of Irgarol 1051 (Boxall et al. 2000). Harino et al. (2004) reported that the Port of Osaka, Japan showed a similar pattern to the marinas of England. Thus, higher concentrations of diuron were observed in marinas and trading ports. On the other hand, Liu et al. (1999) reported that Irgarol 1051 was found more frequently in fishery harbors than in marinas. These findings indicate that the levels of Irgarol 1051 and diuron seem to depend on the utilization form of ports, harbors, or marinas.

3.2.3 Seasonal Variation of Alternative Biocides

Comber et al. (2002) surveyed the concentrations of diuron and Irgarol 1051 in water from the Hamble and Orwell estuaries during the summer and winter seasons. Concentrations of diuron and Irgarol 1051 in water were significantly higher in summer compared with winter. The variation between summer and winter can be attributed to the decreased density of boats in winter. Biselli et al. (2000) reported that a seasonal dependence of Irgarol 1051 concentrations was found in both water and sediment samples, with maxima during the periods of March–May/July–September, whereas during the winter period of December–January low values were encountered, although measurable amounts remained in sediment. Albanis et al. (2002) monitored Irgarol 1051, chlorothalonil, and dichlofluanid in sediment. Maximum and minimum values were observed during the period June–September

Table 3.6 Concentrations of the other alternative biocides in sediment samples

Chemical	Location	Year	Concentrations ($\mu\text{g}/\text{kg}$ dry)	References
Sea nine 211	Southampton, England	2000	<0.1	Thomas et al. (2002)
	Coastal area, Vietnam	2002	0.09–1.3	Harino et al. (2006a)
	The Port of Osaka, Japan	2002–2003	<0.2–2.35 (0.516)	Harino et al. (2004)
	Gulf of Thailand, Thailand	2004	<0.04–0.09 (0.01)	Harino et al. (2006b)
	Otsuchi Bay, Japan	2005	<0.04–150 (6.5)	Harino et al. (2007b)
	Peninsular Malaysia, Malaysia	2006	<0.04–1.7 (0.13)	Harino et al. (2009b)
	Melaka, Malaysia	2006	<0.02–4.2 (0.42)	Harino et al. (2009b)
	Johor, Malaysia	2006	<0.04–0.92 (0.19)	Harino et al. (2009b)
	Nankai Trough, Japan	2006	0.1–1.0 (0.44)	Harino et al. (2009a)
	Suruga Bay, Japan	2006–2007	0.2–1.2 (0.55)	Harino et al. (2009a)
	Tosa Bay, Japan	2007	<0.2	Harino et al. (2009a)
	Maizuru Bay, Japan	2007	<0.04–7.2 (1.1)	Harino et al. (2010)
Chlorothalonil	Blackwater estuary, England	1998–1999	<4.1–46.5 (14.6)	Vouvoulis et al. (2000)
	Southampton, England	2000	<0.1	Thomas et al. (2002)
Dichlofluanid	Blackwater estuary, England	1998–1999	<4.9–688.2 (567)	Vouvoulis et al. (2000)
	Southampton, England	2000	<0.1	Thomas et al. (2002)
	Coastal area, Vietnam	2002	<0.10–13	Harino et al. (2006a)
	Otsuchi Bay, Japan	2005	<0.4–14 (0.44)	Harino et al. (2007b)
	Peninsular Malaysia, Malaysia	2006	<0.1	Harino et al. (2009b)
	Melaka, Malaysia	2006	<0.1	Harino et al. (2009b)
	Johor, Malaysia	2006	<0.1	Harino et al. (2009b)

(continued)

Table 3.6 (continued)

Chemical	Location	Year	Concentrations ($\mu\text{g}/\text{kg dry}$)	References
Pyrethione	Coastal area, Vietnam	2002	<2–420	Harino et al. (2006a)
	Otsuchi Bay, Japan	2005	<8–8.8 (1.2)	Harino et al. (2007b)
	Peninsular Malaysia, Malaysia	2006	<20	Harino et al. (2009b)
	Melaka, Malaysia	2006	<20	Harino et al. (2009b)
	Johor, Malaysia	2006	<20	Harino et al. (2009b)
	Maizuru Bay, Japan	2007	<8	Harino et al. (2010)

and during the winter period (December–February), respectively. Thomas et al. (2001) reported that the concentrations of Irgarol 1051 were low in the yachting season in comparison of those in the off season; however, diuron was contrastingly high.

3.3 Adverse Effect of Alternative Biocides

3.3.1 Toxicity of Each Antifouling Biocide

It is found that high concentrations of alternative biocides were detected in various coastal areas. It is important to clarify how these alternative compounds would impact marine organisms to consider the ecological risk involved by those compounds. Toxicity data of Irgarol 1051 and its degradation compounds (GS26575) are summarized in Tables 3.8 and 3.9.

EC₅₀ values for cyanobacteria, microalgae, periphyton, and cnidarians were in the range of 0.01–23 $\mu\text{g}/\text{l}$ (Mohr et al. 2008; Okamura et al. 2000b; Scarlett et al. 1997, 1999; Lambert et al. 2006). Estimated values of EC₅₀ of crustaceans were higher than those of cyanobacteria, microalgae, periphyton, and cnidarians, which were in the range of 10.8–50,800 $\mu\text{g}/\text{l}$ (Okamura et al. 2000b; Toth et al. 1996; Fernandez-Alba et al. 2002). Crustaceans seemed to be insensitive species for Irgarol 1051. LC₅₀ and NOEC of the common stonewort *Chara vulgaris* for Irgarol 1051 were 0.0168 $\mu\text{g}/\text{l}$ and 0.0005 $\mu\text{g}/\text{l}$, respectively, which seems very sensitive to Irgarol 1051 (Lambert et al. 2006). It is well known that Irgarol 1051 effectively functions by blocking a pivotal step in the electron transport of photosystem II (PS II). The lower EC₅₀ values of microalgae are considered the result of photosynthesis inhibition by Irgarol 1051.

Table 3.7 Concentrations of alternative biocides in biological samples

Chemical	Location	Year	Biota	Concentrations (µg/kg)	References
Irgarol 1051	Coastal area, Vietnam	2002	Clam	<0.10	Harino et al. (2006b)
	Awaji Island, Japan	2003	Mussel	1.1–4.7 (23.1)	Harino et al. (2010)
	Awaji Island, Japan	2003	Oyster	5–35 (11.9)	Harino et al. (2010)
	Gulf of Thailand, Thailand	2004	Mussel	<1	Harino et al. (2006b)
GS26575	Coastal area, Vietnam	2002	Clam	<0.20	Harino et al. (2006a)
	Awaji Island, Japan	2003	Mussel	<0.1	Harino et al. (2010)
	Awaji Island, Japan	2003	Oyster	<0.1–0.2 (0.1)	Harino et al. (2010)
	Gulf of Thailand, Thailand	2004	Mussel	<0.76	Harino et al. (2006b)
Diuron	Coastal area, Vietnam	2002	Clam	<0.20	Harino et al. (2006a)
	Awaji Island, Japan	2003	Mussel	<0.1–0.6 (0.1)	Harino et al. (2010)
	Awaji Island, Japan	2003	Oyster	0.1–0.2 (0.18)	Harino et al. (2010)
	Gulf of Thailand, Thailand	2004	Mussel	<0.64–9.6 (2.8)	Harino et al. (2006b)
Sea nine 211	Coastal area, Vietnam	2002	Clam	<0.10	Harino et al. (2006a)
	Awaji Island, Japan	2003	Mussel	<0.1	Harino et al. (2010)
	Awaji Island, Japan	2003	Oyster	0.1–0.3 (0.14)	Harino et al. (2010)
	Gulf of Thailand, Thailand	2004	Mussel	<0.24–0.24 (0.04)	Harino et al. (2004)
Dichlofluanid	Coastal area, Vietnam	2002	Clam	<0.20	Harino et al. (2006a)

LC₅₀ values of GS26575, which was a degradation product of Irgarol 1051 for microalgae, were in the range of 73–83 µg/l (Gatidou and Thomaidis 2007), and NOEC of GS26575 for the microalgae *Chara vulgaris*, *Myriophyllum spicatum*, and *Apium modiflorum* were ranged from <0.00005 to 0.5 µg/l (Lambert et al. 2006). Thus, the toxicity of GS26575 to microalgae might be greater than that of Irgarol 1051.

Diuron has been used as a herbicide. Observed values of EC₅₀ and LC₅₀ for diuron and its degradation compounds are shown in Table 3.10. EC₅₀ values of diuron for various organisms were 4.3–8600 µg/l (Lambert et al. 2006; Fernandez-

Table 3.8 EC₅₀ and LC₅₀ of Irgarol 1051

Chemical	Taxon	Species	Endpoint	EC ₅₀ (µg/l)	LD _{C50} (µg/l)	References	
Irgarol 1051	Periphyton	Chlorophytes	Mortality	0.34 (135 days)		Mohr et al. (2008)	
		<i>Epithemia adnata</i>	Mortality	0.09 (58 days)		Mohr et al. (2008)	
	Macrophytes	<i>Closterium ehrenbergii</i>	Sporophyte growth	2.5 (5 days)		Okamura et al. (2000b)	
			Embryogenesis	3.6 (5 days)		Okamura et al. (2000b)	
			Gametophyte growth	5.9 (4 days)		Okamura et al. (2000b)	
			Zoospore germination	<2.5 (72 h)		Scarlett et al. (1997)	
			Frond growth	11 (7 days)		Okamura et al. (2000b)	
			Frond growth	8.1 (7 days)		Okamura et al. (2000b)	
			Concospore growth	4.1 (4 days)		Okamura et al. (2000b)	
			Concospore growth	0.6 (4 days)		Okamura et al. (2000b)	
			<i>Chara vulgaris</i>	Photosynthesis	0.0168 (14 days)		Lambert et al. (2006)
			<i>Myriophyllum spicatum</i>	Photosynthesis	>2 (14 days)		Lambert et al. (2006)
			<i>Apium nodiflorum</i>	Photosynthesis	>2 (14 days)		Lambert et al. (2006)
			<i>Zostera marina</i>	Photosynthesis	0.2 (36 days)		Scarkett et al. (1999)
		Cnidarians	<i>Acropora formosa</i>	Photosynthesis	1.3 (10 h)		Jones et al. (2003)
				Photosynthesis	5 (96 h)		Sheikn et al. (2009)
	Crustacea	<i>Galaxea fuscicularis</i>	Mortality	0.33 (92 days)		Mohr et al. (2008)	
			Mortality	0.09 (78 days)		Mohr et al. (2008)	
			Mortality	1.21 (148 days)		Mohr et al. (2008)	
			Mortality	0.11 (148 days)		Mohr et al. (2008)	
			Mortality	1.6 (72 h)		Fernandez-Alba et al. (2002)	
			Mortality		>40,000 (24 h)	Okamura et al. (2000b)	
			Mortality		16,000 (24 h)	Toth et al. (1996)	
		<i>Daphnia magna</i>	Mortality		8,300 (48 h)	Okamura et al. (2000b)	
		<i>Daphnia pulex</i>	Mortality		5,700 (24 h)	Okamura et al. (2000b)	
		<i>Thamnocephalus platyurus</i>	Mortality		12,000 (214 h)	Okamura et al. (2000b)	

Table 3.9 EC₅₀ and LC₅₀ of Irgarol 1051 and GS26575

Chemical	Taxon	Species	Endpoint	EC ₅₀ (µg/l)	LC ₅₀ (µg/l)	References
Irgarol 1051	Crustacea	<i>Selenastrum capricornutum</i>	Mortality	10.8 (72 h)		Fernandez-Alba et al. (2002)
		<i>Daphnia magna</i>	Mortality	7,300 (48 h)		Fernandez-Alba et al. (2002)
		<i>Vibrio fischeri</i>	Mortality	50,800 (15 min)		Fernandez-Alba et al. (2002)
		<i>Balanus amphitrite</i> (larvae)	Mortality		2,200 (24 h)	Bao et al. (2011)
		<i>Elasmopus rapax</i> (juvenile)	Mortality		1,000 (96 h)	Bao et al. (2011)
		<i>Tigriopus japonicus</i> (adult)	Mortality		2,400 (96 h)	Bao et al. (2011)
		<i>Oryzias merastigma</i> (larvae)	Mortality		1,000 (96 h)	Bao et al. (2011)
		<i>Chroococcus minor</i>	Growth	5.7 (7 days)		Bao et al. (2011)
		<i>Synechococcus</i> sp.	Growth	23 (96 h)		Bao et al. (2011)
		<i>Skeletonema costatum</i>	Growth	0.57 (96 h)		Bao et al. (2011)
GS26575	Microalgae	<i>Thalassiosira pseudonana</i>	Growth	0.38 (96 h)		Bao et al. (2011)
		<i>Pyrocystis lunula</i>	Growth	>15,000 (24 h)		Bao et al. (2011)
		<i>Dunaliella teriiolecta</i>	Growth		1.1 (96 h)	Gatidou and Thomaidis. (2007)
		<i>Navicula forcipata</i>	Growth		0.6 (96 h)	Gatidou and Thomaidis. (2007)
		<i>Aiptasia</i> sp.	Growth			Bao et al. (2011)
		<i>Hydroides elegans</i> (larvae)	Mortality		2,600 (48 h)	Bao et al. (2011)
		<i>Oncorhynchus mykiss</i> (juvenile)	Mortality		880 (28 days)	Okamura et al. (2002)
		<i>Chara vulgaris</i>	Photosynthesis	>0.5 (14 days)		Lambert et al. (2006)
		<i>Myriophyllum spicatum</i>	Photosynthesis	>0.5 (14 days)		Lambert et al. (2006)
		<i>Apium nodiflorum</i>	Photosynthesis	>0.5 (14 days)		Lambert et al. (2006)
Microalgae	<i>Dunaliella teriiolecta</i>	Growth		83 (96 h)	Gatidou and Thomaidis (2007)	
	<i>Navicula forcipata</i>	Growth		73 (96 h)	Gatidou and Thomaidis (2007)	

Table 3.10 EC₅₀ and LC₅₀ of diuron and its degradation compounds

Chemical	Taxon	Species	Endpoint	EC ₅₀ (µg/l)	LC ₅₀ (µg/l)	References
Diuron	Ascidians	<i>Myriophyllum spicatum</i>	Photosynthesis	>5 (14 days)		Lambert et al. (2006)
		<i>Apium nodiflorum</i>	Photosynthesis	>5 (14 days)		Lambert et al. (2006)
	Cyanobacteria	<i>Chroococcus minor</i>	Growth	4.7 (7 days)		Bao et al. (2011)
		<i>Synechococcus</i> sp.	Growth	110 (96 h)		Bao et al. (2011)
	Crustacea	<i>Selenastrum capricornutum</i>	Mortality	45 (72 h)		Fernandez-Alba et al. (2002)
		<i>Daphnia magna</i>	Mortality	8600 (48 h)		Fernandez-Alba et al. (2002)
		<i>Balanus amphitrite</i> (larvae)	Mortality		21,000 (24 h)	Bao et al. (2011)
		<i>Elasmopus rapax</i> (juvenile)	Mortality		>3,000 (96 h)	Bao et al. (2011)
	Coral	<i>Tigriopus japonicus</i> (adult)	Mortality		11,000 (96 h)	Bao et al. (2011)
		<i>Acropora tumida</i> (larvae)	Mortality		4,800 (24 h)	Bao et al. (2011)
		<i>Skeletonema costatum</i>	Growth	5.9 (96 h)		Bao et al. (2011)
	Microalgae	<i>Thalassiosira pseudonana</i>	Growth	4.3 (96 h)		Bao et al. (2011)
		<i>Pyrocystis lunula</i>	Growth	43,000 (24 h)		Bao et al. (2011)
		<i>Dunaliella teriolecta</i>	Growth		5.9 (96 h)	Gatidou and Thomaidis (2007)
		<i>Navicula forcipata</i>	Growth		27 (96 h)	Gatidou and Thomaidis (2007)
		<i>Dunaliella teriolecta</i>	Growth		8,500 (96 h)	Gatidou and Thomaidis (2007)
		<i>Hormosira banksii</i>	Germination	6.82 (72 h)		Myers et al. (2006)
<i>Aiptasia</i> sp.		Acute toxicity		>19,000 (96 h)	Bao et al. (2011)	
Polychaete	<i>Hydroides elegans</i> (larvae)	Acute toxicity		16,000 (48 h)	Bao et al. (2011)	
	<i>Hormosira banksii</i>	Rhizoid growth	7.33 (72 h)		Myers et al. (2006)	
Fish	<i>Oryzias merastigma</i> (larvae)	Mortality		7,800 (96 h)	Bao et al. (2011)	
	<i>Oncorhynchus mykiss</i> (juvenile)	Mortality		230 (28 days)	Okamura et al. (2002)	
	<i>Dunaliella teriolecta</i>	Growth		345 (96 h)	Gatidou and Thomaidis (2007)	
DCEMU	Microalgae	<i>Dunaliella teriolecta</i>	Growth		6,381 (96 h)	Gatidou and Thomaidis (2007)
DCA	Microalgae	<i>Dunaliella teriolecta</i>	Growth		6,269 (96 h)	Gatidou and Thomaidis (2007)
DCA	Microalgae	<i>Navicula forcipata</i>	Growth		6,269 (96 h)	Gatidou and Thomaidis (2007)

alba et al. 2002; Bao et al. 2011). LC_{50} of diuron for microalgae was in the range 5.9 to >19,000 $\mu\text{g/l}$ (Bao et al. 2011; Gatidou and Thomaidis 2007). Generally, toxicity of diuron for microalgae was rather strong, which was almost the same level as Irgarol 1051. Diuron is degraded to DCPMU and DCA in the aquatic environment. LC_{50} values of DCPMU and DCA were reported as 345–6,381 $\mu\text{g/l}$ (Gatidou and Thomaidis 2007). Acute toxicities of degradation products of diuron, therefore, were recognized to be weaker than those of diuron.

Table 3.11 represents the observed values of EC_{50} and LC_{50} for sea nine 211 and chlorothalonil. EC_{50} values of chlorothalonil for cyanobacteria, microalgae, and crustaceans were 150–390 $\mu\text{g/l}$, 64.4–190 $\mu\text{g/l}$, and 0.8–28 $\mu\text{g/l}$, respectively (Fernandez-alba et al. 2002; Bao et al. 2011). LC_{50} in polychaetes was in the range of 12 $\mu\text{g/l}$ in 48 h, and LC_{50} of crustaceans were 67–110 $\mu\text{g/l}$ in 96 h (Bao et al. 2011). Estimated values of 48 h LC_{50} (48-h LC_{50}) and 96-h LC_{50} (96-h LC_{50}) of chlorothalonil for polychaetes and crustaceans were 12 $\mu\text{g/l}$ and in the range of 67–110 $\mu\text{g/l}$, respectively (Bao et al. 2011). Observed values of EC_{50} and LC_{50} of sea nine 211 for crustaceans were in the range of 0.42–12 $\mu\text{g/l}$ (Myers et al. 2006) and 14 $\mu\text{g/l}$, respectively (Okamura et al. 2002).

In addition to alternative biocides, which were reviewed in the section on occurrences of antifouling paint, the toxicity data of tolylfluanid (*N'*-dimethyl-*N-p*-tolylsulfamide), TCMTB (2-(thiocyanomethylthio)benzothazole), and zineb (zinc ethylene bis-(dithiocarbamate)) were reported. Estimated values of EC_{50} and LC_{50} for dichlofluanid, tolylfluanid, PTPB, TCMTB, and Zineb are shown in Table 3.12. EC_{50} values of dichlofluanid for crustaceans ranged from 81 to 1050 $\mu\text{g/l}$ (Fernandez-alba et al. 2002; Bellas 2006). Because tolylfluanid has a similar molecular structure to dichlofluanid, the toxicity of tolylfluanid was compared to that of dichlofluanid. EC_{50} values of dichlofluanid and tolylfluanid for embryonic development and larval growth of mussels, sea urchins, and chordata were in the range of 9.9–627 $\mu\text{g/l}$ and 74–405 $\mu\text{g/l}$, respectively (Bellas 2006). On the basis of the literature, it was also found that tolylfluanid had a similar toxicity to dichlofluanid. On the other hand, EC_{50} values of PTPB for algae were 2.2–140 $\mu\text{g/l}$ and EC_{50} for crustaceans were 6.6–100 $\mu\text{g/l}$, respectively (Mochida et al. 2012). LC_{50} values of PTPB for invertebrates and fishes were 54 $\mu\text{g/l}$ and 42–420 $\mu\text{g/l}$, respectively (Mochida et al. 2012; Okamura et al. 2002, 2009). EC_{50} values of TCMTB ranged from 46 to 433 $\mu\text{g/l}$ (Fernandez-alba et al. 2002). Toxicity of zineb for a species of brown algae, Neptune's necklace (*Houmosira banksii*), was high because of its EC_{50} in the range of 0.241–0.49 $\mu\text{g/l}$ (Myers et al. 2006).

Observed values of EC_{50} and LC_{50} for ZnPT and CuPT are shown in Tables 3.13 and 3.14, respectively. Those of EC_{50} and LC_{50} of ZnPT were 0.19–280 $\mu\text{g/l}$ and 4.6–410 $\mu\text{g/l}$, respectively (Bao et al. 2011; Myers et al. 2006; Onzuka et al. 2010); those of EC_{50} and LC_{50} of CuPT were 0.7–50 and 1.3–2000 $\mu\text{g/l}$, respectively (Bao et al. 2011; Okamura et al. 2002; Onzuka et al. 2010).

Table 3.11 EC₅₀ and LC₅₀ of chlorothalonil and sea nine 211

Chemical	Taxon	Species	Endpoint	EC ₅₀ (µg/l)	LC ₅₀ (µg/l)	References
Chlorothalonil	Chordata	<i>Ciona intestinalis</i>	Embryonic development	33 (24 h)		Bellas (2006)
		<i>Ciona intestinalis</i>	Larval attachment	42 (24 h)		Bellas (2006)
	Cyanobacteria	<i>Chroococcus minor</i>	Growth	150 (7 days)		Bao et al. (2011)
		<i>Synechococcus</i> sp.	Growth	390 (96 h)		Bao et al. (2011)
		<i>Elasmopus rapax</i> (juvenile)	Mortality		67 (96 h)	Bao et al. (2011)
	Crustacea	<i>Tigriopus japonicus</i> (adult)	Mortality		91 (96 h)	Bao et al. (2011)
		<i>Oryzias merastigma</i> (larvae)	Mortality		110 (96 h)	Bao et al. (2011)
		<i>Selenastrum capricornutum</i>	Mortality	6.8 (72 h)		Fernandez-Alba et al. (2002)
		<i>Daphnia magna</i>	Mortality	28 (48 h)		Fernandez-Alba et al. (2002)
	Polychaete	<i>Hydroides elegans</i> (larvae)	Mortality		12 (48 h)	Bao et al. (2011)
	Microalgae	<i>Skeletonema costatum</i>	Growth	13 (96 h)		Bao et al. (2011)
		<i>Thalassiosira pseudonana</i>	Growth	4.4 (96 h)		Bao et al. (2011)
		<i>Pyrocystis lunula</i>	Growth	190 (24 h)		Bao et al. (2011)
	Mussel	<i>Mytilus edulis</i>	Embryonic development	8.7 (48 h)		Bellas (2006)
Sea urchin	<i>Paracentrotus lividus</i>	Embryonic development	6.6 (48 h)		Bellas (2006)	
Sea nine 211	Chordata	<i>Ciona intestinalis</i>	Embryonic development	104 (24 h)		Bellas (2006)
		<i>Ciona intestinalis</i>	Larval attachment	43 (24 h)		Bellas (2006)
	Crustacea	<i>Selenastrum capricornutum</i>	Mortality	3 (72 h)		Fernandez-Alba et al. (2002)
		<i>Daphnia magna</i>	Mortality	4 (48 h)		Fernandez-Alba et al. (2002)
		<i>Vibrio fischeri</i>	Mortality	12 (15 min)		Fernandez-Alba et al. (2002)
	Sea urchin	<i>Hormosira banksii</i>	Germination	0.42 (72 h)		Myers et al. (2006)
		<i>Hormosira banksii</i>	Rhizoid growth	0.46 (72 h)		Myers et al. (2006)
		<i>Oncorhynchus mykiss</i> (juvenile)	Mortality		14 (28 days)	Okamura et al. (2002)
		<i>Paracentrotus lividus</i>	Embryonic development	12 (48 h)		Bellas (2006)
	Mussel	<i>Paracentrotus lividus</i>	Larval growth	25 (48 h)		Bellas (2006)
<i>Mytilus edulis</i>		Embryonic development	11 (48 h)		Bellas (2006)	

Table 3.12 EC₅₀ and LC₅₀ of dichlofluanid, tolylfluanid, PTPB, TCMTB, and Zineb

Chemical	Taxon	Species	Endpoint	EC ₅₀ (µg/l)	LC ₅₀ (µg/l)	References
Dichlofluanid	Chordata	<i>Ciona intestinalis</i>	Embryonic development	282 (24 h)		Bellas (2006)
		<i>Ciona intestinalis</i>	Larval attachment	128 (24 h)		Bellas (2006)
	Crustacea	<i>Selenastrum capricornutum</i>	Mortality	133 (72 h)		Fernandez-Alba et al. (2002)
		<i>Daphnia magna</i>	Mortality	1,050 (48 h)		Fernandez-Alba et al. (2002)
		<i>Vibrio fischeri</i>	Mortality	87 (min)		Fernandez-Alba et al. (2002)
		<i>Paracentrotus lividus</i>	Embryonic development	627 (48 h)		Bellas (2006)
Tolyfluanid	Mussel	<i>Mytilus edulis</i>	Embryonic development	81 (48 h)		Bellas (2006)
	Chordata	<i>Ciona intestinalis</i>	Embryonic development	217 (24 h)		Bellas (2006)
		<i>Ciona intestinalis</i>	Larval attachment	95 (24 h)		Bellas (2006)
	Sea urchin	<i>Paracentrotus lividus</i>	Embryonic development	405 (48 h)		Bellas (2006)
		<i>Paracentrotus lividus</i>	Larval growth	9.9 (48 h)		Bellas (2006)
	Mussel	<i>Mytilus edulis</i>	Embryonic development	74 (48 h)		Bellas (2006)
PTPB	Crustacea	<i>Portunus trituberculatus</i>	Mortality	100 (24 h)		Mochida et al. (2012)
		<i>Tigriopus japonicus</i>	Mortality	6.6 (24 h)		Mochida et al. (2012)
	Algae	<i>Artemia salina</i>	Mortality		54 (48 h)	Okamura et al. (2009)
		<i>Chaetocerus calcitrans</i>	Growth	4.4 (72 h)		Mochida et al. (2012)
		<i>Dunaliella tertiolecta</i>	Growth	140 (72 h)		Mochida et al. (2012)
		<i>Skeletonema costatum</i>	Growth	2.2 (72 h)		Mochida et al. (2012)
Fish	<i>Tetraselmis tetraethele</i>	Growth	2.9 (72 h)		Mochida et al. (2012)	
	<i>Pagrus major</i> (juvenile)	Mortality		345 (96 h)	Mochida et al. (2012)	
TCMTB	Crustacea	<i>Fundulus heteroclitus</i> (larvae)	Mortality		420 (96 h)	Mochida et al. (2012)
		<i>Oncorhynchus mykiss</i> (juvenile)	Mortality		42 (28 days)	Okamura et al. (2002)
		<i>Selenastrum capricornutum</i>	Mortality	433 (72 h)		Fernandez-Alba et al. (2002)
	Macroalga	<i>Daphnia magna</i>	Mortality	46 (48 h)		Fernandez-Alba et al. (2002)
		<i>Vibrio fischeri</i>	Mortality	58 (15 min)		Fernandez-Alba et al. (2002)
		<i>Hormosira banksii</i>	Germination	0.49 (72 h)		Myers et al. (2006)
		<i>Hormosira banksii</i>	Rhizoid growth	1.51 (72 h)		Myers et al. (2006)

Table 3.13 EC₅₀ and LC₅₀ of Zn pyrrithione (ZnPT)

Chemical	Taxon	Species	Endpoint	EC ₅₀ (µg/l)	LC ₅₀ (µg/l)	References	
ZnPT	Crustacea	<i>Balanus amphitrite</i> (larvae)	Mortality		210 (24 h)	Bao et al. (2011)	
		<i>Elasmopus rapax</i> (juvenile)	Mortality		29 (96 h)	Bao et al. (2011)	
		<i>Tigriopus japonicus</i> (adult)	Mortality		170 (96 h)	Bao et al. (2011)	
	Cyanobacteria	<i>Skeletonema costatum</i>	Mortality	Mortality	1.6 (72)		Onzuka et al. (2010)
		<i>Chroococcus minor</i>	Growth	Growth	50 (7 days)		Bao et al. (2011)
		<i>Synechococcus</i> sp.	Growth	Growth	22 (96 h)		Bao et al. (2011)
		<i>Acropora tumida</i> (larvae)	Mortality	Mortality		180 (24 h)	Bao et al. (2011)
	Sea anemone		<i>Aiptasia</i> sp.	Mortality	Mortality		Bao et al. (2011)
	Polychaete		<i>Hydroides elegans</i> (larvae)	Mortality	Mortality		Bao et al. (2011)
	Microalgae		<i>Skeletonema costatum</i>	Growth	Growth		Bao et al. (2011)
			<i>Thalassiosira pseudonana</i>	Growth	Growth		Bao et al. (2011)
			<i>Pyrocystis lunula</i>	Growth	Growth		Bao et al. (2011)
			<i>Hormosira banksii</i>	Germination			Myers et al. (2006)
			<i>Hormosira banksii</i>	Rhizoid growth			Myers et al. (2006)
		<i>Dunaliella tertiolecta</i>	Growth			Onzuka et al. (2010)	
		<i>Tetraselmis tetrahele</i>	Growth			Onzuka et al. (2010)	
		<i>Chaetoceros calcitrans</i>	Growth			Onzuka et al. (2010)	
Fish		<i>Oryzias latipes</i> (larvae)	Mortality			Bao et al. (2011)	
		<i>Oncorhynchus mykiss</i> (juvenile)	Mortality			Okamura et al. (2002)	
		<i>Tigriopus japonicus</i>	Mortality			Onzuka et al. (2010)	
		<i>Pagurus major</i>	Mortality			Onzuka et al. (2010)	

Table 3.14 EC₅₀ and LC₅₀ of Cu pyrrithione (CuPT)

Chemical	Taxon	Species	Endpoint	EC ₅₀ (µg/l)	LC ₅₀ (µg/l)	References	
CuPT	Crustacea	<i>Balanus amphitrite</i> (larvae)	Mortality		63 (24 h)	Bao et al. (2011)	
		<i>Elasmopus rapax</i> (juvenile)	Mortality		11 (96 h)	Bao et al. (2011)	
		<i>Tigriopus japonicus</i> (adult)	Mortality		30 (96 h)	Bao et al. (2011)	
	Cyanobacterium	<i>Skeletonema costatum</i>	Mortality	Mortality	1.5 (72 h)		Onduka et al. (2010)
		<i>Chroococcus minor</i>	Growth	Growth	50 (7 days)		Bao et al. (2011)
		<i>Synechococcus</i> sp.	Growth	Growth	22 (96 h)		Bao et al. (2011)
		<i>Acropora tumida</i> (larvae)	Growth	Growth		28 (24 h)	Bao et al. (2011)
		<i>Aiptasia</i> sp.	Mortality	Mortality		2,000 (96 h)	Bao et al. (2011)
	Microalgae	<i>Hydroides elegans</i> (larvae)	Mortality	Mortality		5.7 (48 h)	Bao et al. (2011)
		<i>Skeletonema costatum</i>	Growth	Growth	1.8 (96 h)		Bao et al. (2011)
		<i>Thalassiosira pseudonana</i>	Growth	Growth	0.70 (96 h)		Bao et al. (2011)
		<i>Pyrocystis lunula</i>	Growth	Growth	23 (24 h)		Bao et al. (2011)
		<i>Dunaliella tertiolecta</i>	Growth	Growth	7.3 (72 h)		Onzuka et al. (2010)
		<i>Tetraselmis tetrahele</i>	Growth	Growth	12 (72 h)		Onzuka et al. (2010)
		<i>Chaetoceros calcitrans</i>	Growth	Growth	3.2 (72 h)		Onzuka et al. (2010)
Fish	<i>Oryzias merastigma</i> (larvae)	Mortality	Mortality		8.2 (96 h)	Bao et al. (2011)	
	<i>Oncorhynchus mykiss</i> (juvenile)	Mortality	Mortality		1.3 (28 days)	Okamura et al. (2002)	
	<i>Tigriopus japonicus</i>	Mortality	Mortality	23 (24 h)		Onduka et al. (2010)	
	<i>Pagurus major</i>	Mortality	Mortality	9.3 (96 h)		Onduka et al. (2010)	

3.3.2 Mixture Toxicity

Usually, alternative biocides have been used as mixtures of these compounds. Therefore, the adverse effect of alternative biocides to aquatic organisms must be evaluated as a mixture of compounds that are actually included in antifouling biocide products. Various evaluating methods for the mixture toxicity have been proposed. Here, three representative methods are described.

Mixture toxicity index (MTI) has been often used to evaluate the toxicity of a mixture. To calculate the MTI, toxic unit (TU) was determined by the sum of the ratios of antifouling chemical concentrations to their effective concentrations (24-h LC₅₀) (Verslyche et al. 2003).

$$\text{Expected toxicity (TU)} = \sum C_{mi,a}/C_{mi,e}$$

where $C_{mi,a}$ is nominal concentration; $C_{mi,e}$ is effective concentration (24-h LC₅₀).

The MTI (mixture toxicity index) was determined, according to the following equation, on the basis of the methodology originally described by Konemann (1981).

$$\text{MTI} = 1 - (\log M / \log M0)$$

where M is the sum of the concentrations that was expressed as equal fractions of the 24-h LC₅₀ of each component ($M = \sum \text{TU}_i$); $M0$ is M divided by the largest fraction in the mixture ($M0 = M / \max(\text{TU}_i)$). $\text{MTI} = 0$ gives antagonism and no addition, partial addition gives $0 < \text{MTI} < 1$, strict addition and synergism gives $\text{MTI} > 1$.

Koutsaftis and Aoyama (2007) evaluated the effect of the binary mixtures for brine shrimp, *Artemia salina*, by MTI. The binary mixtures, two agents consisting of 0.2, 0.4, 0.5, and 0.8 times the 24-h LC₅₀ for one chemical with the other chemical constituting the remaining percentage by its 24-h LC₅₀ times the fraction amount, determined the combination ratio. For the mixtures of ZnPT and CuPT, all propositions of mixtures indicated synergistic effect. The mixtures of chlorothalonil and CuPT gave antagonistic effect in all propositions of mixture. For chlorothalonil and ZnPT, CuPT and diuron, diuron and ZnPT, and diuron and chlorothalonil, effects for brine shrimp depend on the proportions of the mixture.

Fernandez-Alba et al. (2002) evaluated the toxicity of mixtures using *Vibrio fischeri*, *Selenastrum capricornotum*, and *Daphnia magna*. A binary mixture of Irgarol 1051 and diuron, and Irgarol 1051 and TCMTB, showed the synergistic effect for these three species. A binary mixture of sea nine 211 showed antagonistic effect for *V. fischeri* and additive effect for *S. capricornotum* and *D. magna*. Although a binary mixture of Irgarol 1051 and chlorothalonil showed synergistic effect for *V. fischeri* and *S. capricornotum*, they showed antagonistic effects for *D. magna*. A binary mixture of Irgarol 1051 and dichlofluanid showed additive

effect for *V. fischeri* and *S. capricornotum* and showed synergistic effect for *D. magna*. Thus, effects of mixtures were various for organisms.

In the other method, Abbotts' formula has been often used to compare expected and observed inhibitions:

$$C_{exp} = A + B - (AB/100)$$

where C_{exp} is expected inhibitions (%); A or B is inhibitions caused when compounds act alone.

The ratio of inhibition (RI) for each mixture of compounds was calculated as follows.

$$RI = \text{observed inhibition}/C_{exp}$$

where RI values > 1 are synergism; RI values $= 1$ are additivity; RI values < 1 are antagonism.

Gatidou and Thomaidis (2007) evaluated the effect of a mix of the antifouling biocides and their metabolites or copper by this method. A binary mixture of Irgarol 1051 and GS26575 revealed additive effects on the growth of a species of green alga, *Dunaliella tertiolecta*. Coexistence of Irgarol 1051 and copper had shown additivity as well. A binary mixture of GS26575 and copper resulted in additive effects when a low concentration of copper (2000 $\mu\text{g/l}$) combined with GS26575 and synergism when a high concentration of copper (4000 $\mu\text{g/l}$) was used. Combination of diuron with either DCPMU or DCA resulted in synergistic effects. Copper, when either diuron or DCPMU was used together, showed antagonistic effects. A binary mixture of both mixtures (Irgarol 1051-GS26575 and diuron-DCA) for a species of diatoms, *Navicula forcipata*, were similar to those observed for *Dunaliella tertiolecta*. All binary concentration levels of diuron and DCA were found to show synergistic effects for *Navicula forcipata*.

Mochida et al. (2006) investigated the joint toxicity by using LC_{50} values of pyrithiones and copper. As a result, the joint toxicity of the ZnPT and Cu mixture was more than the additive toxicities of CuPT and Cu in toy shrimp, *Heptacarpus futilirostris*.

3.4 Conclusion

After the worldwide ban of TBT, various alternative biocides have been detected in the marine environment.

Fortunately, detection frequencies of alternative biocides in biological samples were low; however, higher concentrations of these alternative biocides were detected in water and sediment. Although the concentrations of alternative biocides detected in coastal water samples from various areas were lower than their toxicity level for aquatic organisms, these compounds were transferred to deep-sea areas.

Some of the alternative biocides were easily degraded in water; however, little information has been available for the behavior and toxicity of degradation products in the aquatic environment. Further studies are needed to clarify the fate and effect of alternative biocides containing the degradation products.

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