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Occurrence of antifouling biocides in Japan and Southeast Asia: The survey for 10 years

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Abstract— The concentrations of organotin (OT) compounds were surveyed in four coastal areas of Japan (the Port of Osaka, Maizuru Bay, Otsuchi Bay and Tanabe Bay). Tributyltin (TBT) concentrations in water and sediment from the Port of Osaka were higher in a marina and a mooring for small- and medium-hull vessels than the other areas. Some alternative compounds were detected in the Port of Osaka; especially, diuron concentration was the highest. OTs concentrations in Maizuru Bay are lower among those coastal areas in Japan. Diuron and Irgarol 1051 were detected in the sediment from Maizuru Bay. Concentrations of Diuron and Irgarol 1051 in the vicinity of a shipyard and a small fishing port from Otsuchi Bay were dramatically high in comparison with the other sites. Copper pyrithione and Dichlofluanid in addition to Diuron and Irgarol 1051 were also detected in sediment of the area of a small fishing port from Otsuchi Bay. OTs concentration in Tanabe Bay is the highest among the coastal areas in Japan and the concentrations of alternative compounds were lower than those of OT compounds.

OTs concentrations were surveyed in the deep sea environment. In the sediment core of 0–30.5 cm from Suruga Bay, the BTs and PTs concentrations were constant between 0–15 cm and subsequently the concentration of these compounds increased, showing the peak between 18–19 cm. After the peak, TBT and TPT concentrations decreased. In Tosa Bay, BTs concentrations decreased with the depth, suggesting the spread of OTs contamination from coastal waters. OTs and alternative biocides were detected even in the sediment and organisms from Nankai Trough (4000 m in depth).

The highest concentration of TBT in Thailand was detected at an industrial area with shipyards. On the other hand, TPT was not detected in the sediment. The concentrations of TBT in some mussel samples from Thailand were higher than TARL (Tolerable average residue levels). Among alternative biocides, Diuron was only detected. Concerning the marine mammals, the concentrations of BTs were high in the order of whales>dugongs>dolphins and the concentration of PTs in whales was higher than that in dolphins and dugongs. The concentrations of MBT, DBT and TBT in sediment from the coastal water of Peninsular Malaysia were measured. TBT concentrations in Johor Strait were higher than those in other sites in Peninsular Malaysia. Although TBT concentrations in sediment from Vietnam were low, Sea Nine 211 concentrations were high.

Thus, the contamination of antifouling biocides has expanded widely from the coastal area to deep-sea environments in Japan and Southeast Asia. The necessity of the continuous research is therefore suggested.

Key words: organotin, alternative biocides, water, sediment, biological samples

Introduction

Organotin (OT) compounds have been utilized as active biocides in antifouling paints since the early 1960s, and have caused deleterious effects such as decrease in thickness of oyster shell, feminization in an amphipod and endocrine disruption of non-target marine organisms (Laughlin and Linden 1985, Ohji et al. 2002, 2003, Bryan and Gibbs 1991). As the result, the releases of organotin compounds have caused the decreasing of aquatic resources. Environmental researches have indicated OT contamination of the marine environment on a worldwide scale (Clark et al. 1988). In the 1980s, the use of tributyltin (TBT) was regulated in some developed countries such as England, France and the USA. In Japan, bis(tributyltin)oxide (TBTO) has been banned under "the Law Concerning the Examination and Regulation of Manufacture etc. of Chemical Substances" in 1990, and the uses of 7 triphenyltin (TPT) and 13 TBT species, excluding TBTO, have permitted with notification by this law.

In spite of the regulation for OT, these compounds have been still detected at higher concentrations in water, sediment and biota from harbours, marinas and estuaries, particularly where boat activity is high and water movement is restricted (Harino et al. 1998a). In 2001, the International Maritime Organization (IMO) adopted the International Convention on the Control of Harmful Antifouling Systems (AFS Convention), which prohibits the use of OTs as active ingre-

dients in antifouling systems for ships, and this convention was ratified in 2008. 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. It is reported that representative alternative compounds such as Sea nine 211, Diuron, Irgarol 1051, Dichlofluanid have detected in water and sediment from various countries (Harino 2004).

Thus, the contaminations by not only OTs but also alternative compounds are prevailed in the coastal water. Authors have been researched the antifouling biocides in Japan and Southeast Asian countries (Thailand, Malaysia and Vietnam) for 10 years. In this paper, on the basis of the authors' research, contaminations by antifouling biocide are reviewed.

Sampling area and analytes through 10-year survey

Sampling areas in Japan are shown in Fig. 1. The Port of Osaka, Maizuru Bay, Otsuchi Bay and Tanabe Bay were selected as the sampling areas from the coastal area of Japan. Furthermore, as the deep sea areas, Suruga Bay, Tosa Bay and Nankai Trough were selected. Sediment and mussel samples were taken in Thailand, Malaysia and Vietnam from the Southeast Asian countries (Fig. 2). In these areas, monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPT), diphenyltin (DPT) and triphenyltin (TPT) as OTs and Sea Nine 211, Diuron, Dichlofluanid, Irgarol 1051, M1 and pyrithiones as antifouling biocides were measured in these samples (Figs 3 and 4).

Contamination by antifouling biocides in the coastal area from Japan

Harino et al. (1999, 2004) monitored butyltin (BT) and phenyltin (PT) compounds in water, sediment, plankton and mussels from the Port of Osaka between 1989 and 2000. TBT concentrations in water, plankton and mussels decreased remarkably in marina and the mooring places in a zone of poor flushing during this period. Although high levels of TPT were detected in water, plankton and mussel between 1989 and 1991, after that, TPT have not been detected. On the other hand, TBT and TPT in sediment were constant in this period. Harino et al. (2010) reported the current levels of TBT in the Port of Osaka (Table 1). TBT in water from the Port of Osaka showed higher concentrations in a marina and a mooring for small- and medium-hull vessels. The concentration of TBT in water was above the levels which cause imposex of dog whelk (*Nucella lapillus*) and abnormal growth of oyster (*Crassostrea gigas*) (Gibbs et al. 1986, 1987, Alzieu 1986). Harino et al. (2010) was reported that the

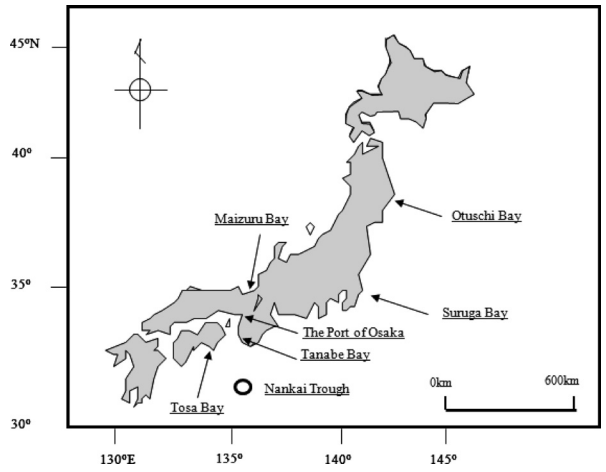

Fig. 1. Study area in Japan.

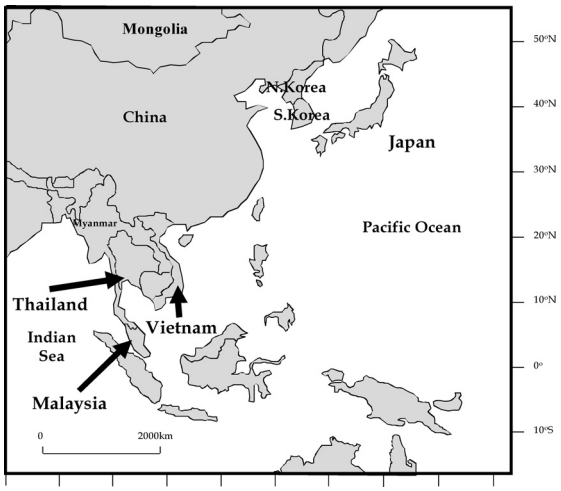

Fig. 2. Study area in Southeast Asia.

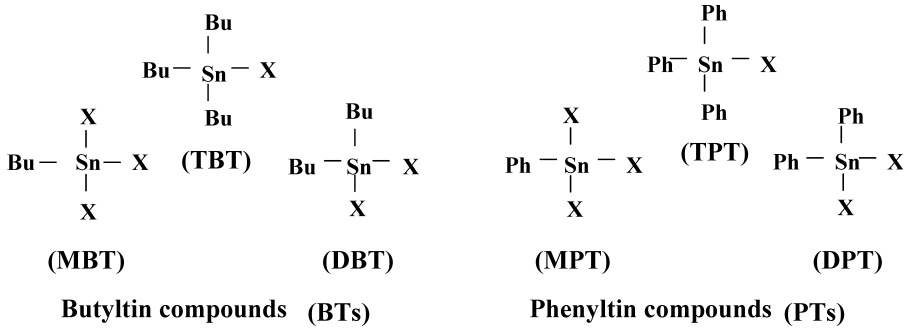

Fig. 3. The structure of organotin compounds.

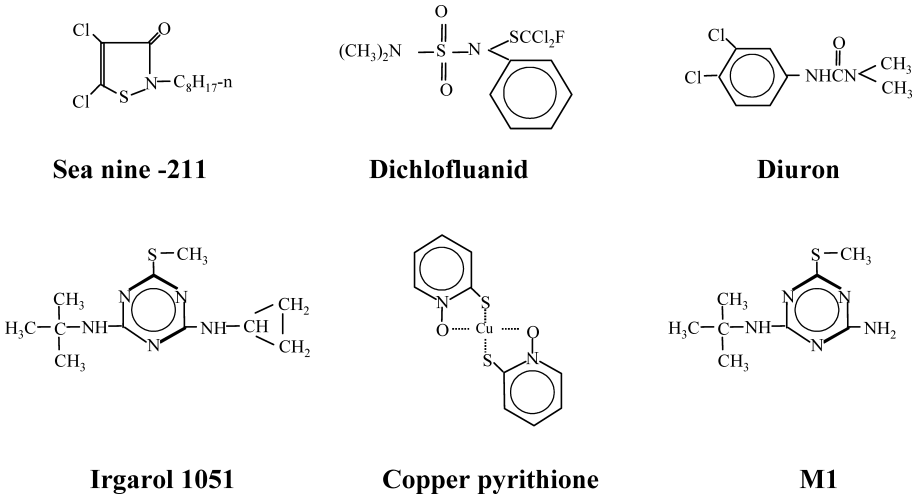

Fig. 4. The structure of representative alternative compounds.

Table 1. Concentrations (μg kg^{-1} dw) of organotin compounds in sediment from Japan. Values in parentheses represent average.

Sampling area		Sampling year	MBT	DBT	TBT	MPT	DPT	TPT	References
The port of Osaka	coastal water	2005–2006	2.2–587 (93)	0.8–725 (103)	0.6–240 (58)	0–667 (62)	0.1–518 (64)	0–270 (26)	Harino et al., 2010
Maizuru Bay	coastal water	2007	4.8–27 (11)	1.8–30 (9.1)	0.9–11 (3.4)	5.9–44 (16)	0.9–39 (16)	0.2–19 (7.5)	Eguchi et al., 2009
Otsuchi Bay	coastalwater	2005	0.3–118 (38)	1.5–80 (15)	0–201 (28)	0–189 (43)	0–28 (4.8)	0–88 (11)	Harino et al., 2007a
Otsuchi Bay	coastalwater (near the shipyard)	2005	32–3349 (306)	14–3419 (259)	19–13718 (964)	15–5202 (454)	2.0–686 (56)	2.3–3532 (300)	Harino et al., 2007a
Tanabe Bay	coastal water	2005–2006	0.2–1886 (376)	2.3–976 (223)	2.6–46411 (5675)	0–293 (90)	0.7–5542 (684)	0.9–6852 (1063)	Harino et al., 2010
Suruga Bay	Water depth; 800 m	2007	36–54 (45)	2.1–3.0 (2.6)	1.5–2.9 (2.2)	4.2–18 (13)	0.3–0.7 (0.5)	0.3–1.8 (0.8)	Harino et al., 2009a
Tosa Bay	Water depth; 202 m	2007	5.4–6.7 (6.1)	1.1–3.5 (2.3)	0.2–1.3 (0.7)	0.6 (0.6)	0.1 (0.1)	<0.1 (<0.1)	Harino et al., 2009a
	Water depth; 100 m	2007	5.8–9.4 (7.0)	5–8.5 (7.2)	0.5–2.6 (1.1)	1.4 (1.4)	0.2 (0.2)	0.1–0.6 (0.3)	Harino et al, 2009a
	Water depth; 50.4 m	2007	8.4–33 (17)	2.4–14 (5.8)	1.6–41 (7.2)	1–15 (6.1)	0.1–0.6 (0.4)	0.1–1.1 (0.3)	Harino et al, 2009a
Nankai Trough	Water depth; 3553–3571 m	2001	9–12 (11)	12–23 (18)	4–5 (4.5)	8–33 (21)	13–21 (17)	<1–7 (3.5)	Harino et al., 2005b
	Water depth; 4010 m	2007	28–77 (51)	1.1–2.6 (1.7)	0.9–5.0 (2.1)	9.7–13 (11)	0.3–0.7 (0.4)	0.2–1.3 (0.5)	Harino et al., 2009a

higher concentration of TBT in sediment was also observed in a marina and a mooring for small- and medium-hull vessels. It was reported that half-lives of TBT in the sediment were in the range of 360–775 days (Dowson et al. 1993). It is also reported that the half-lives of TBT in water and sediment were 6–19 days and several months, respectively (Seligman et al. 1986, Maguire et al. 1985). Harino et al. (1998b) reported that the time when OTs began to be used as an antifouling paint was coincident the time estimated from the profile of sediment core, showing that OTs in sediment are not degraded for a long time. It was therefore concluded that large amounts of TBT have been deposited in sediment over a long period in a marina and a mooring for small- and medium-hull vessels. The levels of TBT in mussels from a marina and a mooring for small- and medium-hull vessels were also high. TPT was not detected in water from the Port of Osaka (Harino et al. 2010). The concentrations of TPT in sediment, plankton and mussels were low in comparison with TBT.

The concentration of alternative biocides in the Port of Osaka was reported by Harino et al. (2005a). The concentrations of Sea-Nine 211 in water ranged from <0.0003 to

Table 2. Concentrations ($\mu g\,kg^{-1}$ dw) of alternative biocides in sediment from Japan. Values in parentheses represent average.

Sampling area		Sampling year	Sea Nine 211	Diuron	Dichlofluanid	Irgarol1051	M1	Pyrithions	References
The port of Osaka	coastal water	2005–2006	<0.1–107 (12)	0.4–895 (111)	<0.1–0.8 (0.1)	0.5–23 (4.7)	<0.1–8.2 (1.3)	<3 (<3)	Harino et al., 2010
Maizuru Bay	coastal water	2007	<0.1–7.2 (0.9)	<0.1–12 (5.9)	0.1 (0.1)	<0.1–9.8 (3.7)	0.1 (0.1)	<3 (<3)	Eguchi et al., 2009
Otsuchi Bay	coastal water	2005	<0.1–0.3 (0.1)	0.1–18 (3.2)	0.1–14 (1.0)	<0.1–21 (1.7)	0.1–0.5 (0.1)	<3–22 (4.3)	Harino et al., 2007a
	coastal water (near the shipyard)	2005	0.1–145 (12)	1.0–534 (45)	<0.1–0.1 (0.1)	0.1–103 (7.6)	0.1–0.5 (0.1)	3.0–8.8 (3.7)	Harino et al., 2007a
Tanabe Bay	coastal water	2005–2006	<0.1–0.3 (0.1)	0.1–2.1 (0.7)	0.10 (0.1)	<0.1–0.1 (0.1)	0.1 (0.1)	<3 (<3)	Harino et al., 2010
Suruga Bay	Water depth; 800m	2007	0.2–1.2 (<0.1)	0.4–1.5 (<0.1)	<0.1 (<0.1)	0.1 (0.1)	<0.1 (<0.1)	<3 (<3)	Harino et al., 2009b
Tosa Bay	Water depth; 202m	2007	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<3 (<3)	Harino et al., 2009b
	Water depth; 100m	2007	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1–0.1 (<0.1)	<0.1 (<0.1)	<3 (<3)	Harino et al., 2009b
	Water depth; 50.4m	2007	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1–0.2 (0.1)	<0.1 (<0.1)	<3 (<3)	Harino et al., 2009b
Nankai Trough	Water depth; 4010m	2007	0.1–1.0 (0.4)	<0.2–0.5 (0.5)	<0.1 (<0.1)	<0.1–0.2 (0.1)	<0.1 (<0.1)	<3 (<3)	Harino et al., 2009b

$0.004\,\mu g\,l^{-1}$) (means $0.002\,\mu g\,l^{-1}$), which were lower than the coastal areas of England and Greece and were lower than LC50 values of 2.7–$20.5\,\mu g\,l^{-1}$ for fish. The levels of Sea-Nine 211 in the sediment from the port of Osaka were the highest among our studied areas (Table 2). The concentrations of Diuron in water were ranged from <0.0007 to $1.54\,\mu g\,l^{-1}$) (means $0.126\,\mu g\,l^{-1}$)) and were a little higher among the coastal areas of England. The concentrations of Diuron in sediment from the port of Osaka were higher in comparison with the other areas as well as water (Table 2). Irgarol 1051 in water was detected in the range of <0.0008–$0.267\,\mu g\,l^{-1}$ (means $0.013\,\mu g\,l^{-1}$) and is a little lower than the coastal areas from England. The concentrations of Irgarol 1051 detected in the Port of Osaka were have the possibility of growth inhibition for green macroalga and long-term effects on the periphyton communities. The levels of Irgarol 1051 in sediment from the port of Osaka were within the results in the other sites (Table 2). The levels of antifouling biocides in water were high in the order of Diuron >Irgarol 1051=M1>Sea-Nine 211.

The high concentrations of Sea-Nine 211, Diuron and Irgarol 1051 were observed in the locations where small and medium hull vessels moor and poor flushing zone exist.

Eguchi et al. (2010) reported the concentrations of OT compounds in water, sediment and mussels from Maizuru Bay. TBT concentrations in Maizuru Bay are low in comparison with the other coastal waters in Japan. Drastic differences of TBT concentrations were not observed among the sampling sites of Maizuru Bay. PT compounds were not detected in water samples. TBT concentrations in sediment from Maizuru bay were lower than those in other areas that we have studied. From the concentrations of TBT and TPT in blue mussel from Maizuru Bay (Table 3), a tolerable average residue levels (TARL) was estimated at $74.8\,\mu g\,kg^{-1}$ wet weight (ww) from a tolerable daily intake (TDI) of 0.25 TBTO $mg\,kg^{-1}$ body weight day^{-1}. TBT concentrations which were detected in blue mussel samples were lower value in comparison with TARL. Acceptable concentration of TPT was calculated using ADI (acceptable daily intake) instead of TDI. Acceptable concentration of TPT was $127\,\mu g\,kg^{-1}$ ww. The concentrations of TPT in blue mussel samples also lower than the TARL. TBTs in blue mussel samples were similar levels in various sampling sites of Maizuru Bay and the ratios of degradation product of TBT and TPT were higher than parent compounds, indicating that TBT is not applied on ship hull at the present day.

The alternative biocides in water samples from Maizuru Bay were investigated by Eguchi et al. (2010). Although Sea Nine 211, M1 and pyrithiones were not detected, Diuron and Irgarol 1051 were detected at the range of 0.010–$0.257\,\mu g\,l^{-1}$ and 0.002–$0.018\,\mu g\,l^{-1}$. The concentrations of Diuron were high in the shipping road and near the shipyard, while, the concentration of Irgarol 1051 were high in the fishing port.

OTs concentrations in Otsuchi Bay have been measured since 1994 (Harino et al. 2003). No changes of TBT in water and mussel samples were observed, while, the concentrations in sediment decreased slightly. Higher concentrations of TBT and TPT in sediment were observed in the vicinity of the shipyard (Table 1) (Harino et al. 2007). A higher concentration of TPT in comparison with TBT was detected in a small

Table 3. Concentrations ($\mu g\,kg^{-1}$ ww) of organotin compounds in biological samples from Japan. Values in parentheses represent average.

Sampling area	Sampling year	Biological samples		MBT	DBT	TBT	MPT	DPT	TPT	References
Maizuru Bay	2007	Bivalves	*Mytilus galloprovincialis*	1.6–4.2 (2.9)	1.2–3.8 (1.8)	2.4–9.3 (3.8)	1.3–12 (3.9)	0.2–6.7 (1.0)	0.2–13 (1.9)	Eguchi et al., 2009
Otsuchi Bay	2005	Bivalves	*Mytilus galloprovincialis*	4–32 (17)	3–92 (35)	3–287 (88)	<1 (<1)	<1–13 (5.5)	<1–80 (53)	Harino et al., 2007a
Nankai Trough	2001	Bivalves	*Clyptogena nautilei*	1.4–52 (9.7)	2.3–35 (14)	1.5–3.1 (2.0)	13–48 (25)	<1 (<1)	<1 (<1)	Harino et al., 2005b
			Clyptogena tsubasa	6.3–7.9 (7.1)	9.4–11 (10)	1.1–1.5 (1.3)	29–30 (30)	<1 (<1)	<1 (<1)	Harino et al., 2005b
		Gastropods	*Colliloconcha nankaiensis*	9.7–108 (54)	4.7–59 (24)	2.1–34 (11)	73–327 (206)	<1–1.4 (0.6)	<1–12 (4.8)	Harino et al., 2005b
		Galatheid crabs	*Munidopsis Albatrossae (famale)*	9.7 (9.7)	5.6 (5.6)	2.7 (2.7)	140 (140)	<1 (<1)	26 (26)	Harino et al., 2005b
			Munidopsis subsquamosa (female)	9.7 (9.7)	5.9 (5.9)	0.8 (0.8)	179 (179)	1.0 (1.0)	5.9 (5.9)	Harino et al., 2005b
		Sea cucumber	*Psychropotes verrucosa*	44 (44)	9.4 (9.4)	3.1 (3.1)	354 (354)	5.4 (5.4)	3.0 (3.0)	Harino et al., 2005b

fishing port. OT concentrations in mussels decreased with the distance from the shipyard.

Concentrations of Diuron and Irgarol 1051 in sediment from the vicinity of a shipyard and a small fishing port were dramatically high in comparison with the other sites. Copper pyrithione and Dichlofluanid in addition to Diuron and Irgarol 1051 were also detected in the area of a small fishing port (Table 2).

The concentration of TBT and TPT in sediment from Tanabe Bay was in the range of 3–46,411 $\mu g\,kg^{-1}$ dw and 1–6851 $\mu g\,kg^{-1}$ dw, respectively. Among the coastal areas of Japan which were reviewed in this paper, highest concentrations of TBT and TPT were found in Tanabe Bay which have a small fishing area and farms (Table 1), suggesting that a lot of organotin (OT) compounds was used in the past.

Generally, although alternative biocides were detected, their concentrations are lower than those of OT compounds (Tables 1 and 2). The concentrations of Diuron were the highest among alternative compounds.

Contamination by antifouling biocides in the deep sea area near Japan

The concentrations of OTs were surveyed in the sediment from Suruga Bay at the depth of 800 m (Table 1) (Harino et al. 2009a). Significant differences of the TBT and TPT concentrations in subsurface sediment at 800 m of water depth were not observed. OT concentrations in the sediment core of 0–30.5 cm were investigated (water depth: 850 m). The BTs and PTs concentrations were constant between 0–15 cm and subsequently the concentration of these compounds increased. The peaks of the BTs and PTs concentrations were observed between 18–19 cm. Subsequently, TBT and TPT concentrations were decreased. The vertical distribution of PTs showed a similar trend to BTs.

Alternative biocides were detected in the subsurface sediment from Suruga Bay (water depth: 800 m) (Table 2) (Harino et al. 2009a). The concentrations of Sea Nine 211, Diuron and Irgarol 1051 were in the range of 0.2–1.2, 0.4–1.5 and 0.1 $\mu g\,kg^{-1}$ dw, respectively. The concentrations of Sea Nine 211 which was also detected in Suruga Bay were within those in the coastal waters. The levels of Diuron in the deep-sea environment were lower than those in coastal waters. The Irgarol 1051 concentrations in the deep sea environment were lower in comparison with those of previous reports on coastal waters. Irgarol 1051 in the sediment core of 0–30.5 cm showed a different profile from the BTs and PTs. The concentrations of Irgarol 1051 decreased up until a depth of 9 cm in the core, and then at a depth of 10 cm and under, the Irgarol 1051 values were near the detection limit, suggesting the recent input of this contaminant.

Harino et al. (2009a) analyzed the OT compounds in sediment samples which were taken at a water depth of 50 m, 100 m and 200 m from Tosa Bay (Table 1). The BTs concentrations decreased as the water depth became deeper, suggesting the spread of OTs contamination from coastal waters. Of all the BTs compounds, the ratio of each BTs compound was in the following order from high to low (MBT>DBT >TBT). On the other hand, the PTs concentrations in subsurface sediment were at the values near the detection limit in the deep sea of Tosa Bay. BTs concentrations decreased as the core depth becomes deeper, but the PTs concentrations were constant throughout this sediment core. Irgarol 1051 was the only alternative compound detected at the concentrations of <0.1–0.2 $\mu g\,kg^{-1}$ dw (Table 2).

TBT and TPT compounds was detected at the concentration of 4.5 and 3.5 $\mu g\,kg^{-1}$ dw, respectively, in sediment from Nankai Trough (Table 1) (Harino et al. 2005). OTs were detected in gastropods (*Colliloconcha nankaiensis*), sea cucumbers (*Psychropotes verrucosa)*, galatheid crabs (*Munidopsis albatrossae* and *Munidopsis subsquamosa*) and bivalves (*Clyptogena tsubasa* and *Clyptogena nautilei*) collected from the Nankai Trough (water depth about 3000 m). The organisms that use organic matter chemosynthesized by symbiotic bacteria and those dependent on photosynthesis carried out near the surface by phytoplankton existed in deep sea environment. No difference in BTs or TBT concentration are observed between the two groups, but PTs and TPT concentrations in the organisms that depend on photosynthesis were higher than those in the chemosynthesis-dependent organisms. Although no relationship between BTs and TBT concentration and trophic level was observed, PTs and TPT concentrations generally increased with increase of trophic level.

Sea Nine 211, Diuron and Irgarol 1051 were detected in the ranges of 0.1–1.0, <0.2–0.5 and <0.1–0.2 $\mu g\,kg^{-1}$ dw, respectively (Table 2) (Harino et al. 2005). The concentrations of these compounds were lower than those from the coastal areas. However, it is found that deep sea area has already been contaminated by alternative biocides.

Contamination by antifouling biocides in Thailand

The survey of antifouling paints was conducted along the coastal areas of Thailand (Harino et al. 2006a). Sediment of Thailand was contaminated by TBT (Table 4). The highest concentration of TBT (1,246 $\mu g\,kg^{-1}$ dw) in sediment was displayed at an industrial area with shipyards. The concentrations of PTs in sediment were in the range of 0.9–35 $\mu g\,kg^{-1}$ dw. The highest concentration in green mussel (*Perna viridis*) was observed from the station in an aquaculture area with heavy cargo shipping activities. The concentrations of TBT in green mussels ranged from 4 to 45 $\mu g\,kg^{-1}$ ww. The concentrations of TBT in some of green mussel samples were higher than TARL. Meanwhile, the detection frequencies of TPT were low in the green mussels and the PTs concentrations in the most of sampling sites were close to the detection limit.

The concentrations in marine mammals from Thailand were surveyed. The concentrations of BTs and PTs in whales (Bryde's whales, false killer whales, pygmy killer whales, short-finned pilot whales and sperm whales) were higher than those in mussels from the coastal area of Thailand (Harino et al. 2007). BT concentrations were generally higher in liver and lower in lung. TPT concentrations were higher in liver and blubber, and lower in lung. Proportion of TBT's degradation products, monobutyltin (MBT), dibutyltin (DBT), in liver of whales was higher than that of TBT. TPTs were the dominant species in liver. Concentrations of BT and PT compounds were measured in the organs and tissues of dugongs (*Dugong dugon*) from the coastal waters of Thailand (Harino et al. 2007). Concentrations of BTs and PTs were in the range of 14–14,468 and <1–30 $\mu g\,kg^{-1}$ ww (detection frequency: 79%), respectively. Although concentrations of BTs in dugongs were higher than reported concentrations in cetaceans and pinnipeds, PTs were lower in dugongs. OT concentrations in seven species of dolphins (bottlenose dolphin, finless porpoise, Indo-Pacific humpbacked dolphin, long-beaked common dolphin, pantropical spotted dolphin, spinner dolphin and striped dolphin), that stranded on the coast of Thailand, were measured (Harino et al. 2008). BT and PT compounds in tissues and organs of dolphins were detected in the range of 16–1,152 and <1–62 $\mu g\,kg^{-1}$ ww, respectively. The highest concentration of TBT was generally observed in liver among the tissues and organs. The concentrations of TPT were lower than those of TBT. OTs concentrations in tissues and organs were compared among dolphins, whales and dugongs stranded on the coasts of Thailand. The concentrations of BTs were high in the order of whales>dugongs>dolphins, and the concentration of PTs in whales was higher than that in dolphins and dugongs.

The detection frequencies and concentrations of Sea

Table 4. Concentrations of organotin compounds in sediment ($\mu g\,kg^{-1}$ dw) and biota ($\mu g\,kg^{-1}$ ww) from Southeast Asia. Values in parentheses represent average.

Location	Sampling date	sample	MBT	DBT	TBT	MPT	DPT	TPT	Reference
Thailand	2004	sediment	1.0–293 (56)	0.7–368 (57)	1.6–1246 (156)	0.3–9.5 (2.0)	0.3–5.6 (1.1)	0.3–29 (7.0)	Harino et al., 2006a
Malaysia	2007	sediment	4.1–542 (126)	1.1–232 (57)	0.7–492 (97)	<0.1–121 (40)	0.4–29 (9.9)	0.1–34 (11)	Harino et al., 2009b
Vietnam	2002	sediment	<0.1–11 (1.5)	0.6–4.6 (1.7)	0.9–28 (7.3)	2.2–5.8 (3.4)	0.1–3.6 (0.6)	0.1–0.4 (0.1)	Midorikawa et al., 2004
Thailand	2004	Green Mussel (*Perna viridis*)	8–20 (13)	4–9 (6)	4–45 (16)	10–49 (24)	<1–52 (14)	<1–5 (1)	Harino et al., 2006a
Vietnam	2002	Clam (*Meretrix spp.*)	0.1–44 (9.3)	0.5–10 (2.4)	1.4–56 (9.2)	0.2–11 (2.9)	<0.1–0.7 (0.1)	<0.1–3.1 (0.8)	Midorikawa et al., 2004

Table 5. Concentration of alternative biocides in sediment ($\mu g\,kg^{-1}$ dw) and biota ($\mu g\,kg^{-1}$ ww) from Southeast Asia. Values in parentheses represent average.

Location	sample	sampling date	Sea Nine 211	Diuron	Dichlofluanid	Irgarol 1051	M1	Pyrithions	Reference
Thailand	sediment	2004	<0.04–0.09 (0.04)	0.07–25 (3.5)		0.03–3.2 (0.15)	0.03–4.9 (0.63)		Harino et al., 2006a
Malaysia	sediment	2007	<0.02–1.7 (0.09)	<0.04–4.8 (0.71)	<0.10	<0.04–14 (1.7)	<0.09	<2	Harino et al., 2007b
Vietnam	sediment	2002	<0.09–1.3 (0.45)	0.11–3.0 (1.2)	<0.10–13 (2.8)	<0.05–4.0 (0.78)	<0.09–0.43 (0.16)	<2–420 (43)	Harino et al., 2006b
Thailand	Green Mussel (*Perna viridis*)	2004	<0.24–0.12 (0.09)	<0.64–9.6 (2.8)		<0.76–0.22 (0.15)	<0.24–0.85 (0.38)		Harino et al., 2006a
Vietnam	Clam (*Meretrix spp.*)	2002	<0.1	<0.2	<0.2	<0.1	<0.2		Harino et al., 2006b

Nine 211 in sediment were low. The range of Diuron concentrations in sediment from Thailand (0.07–25 $\mu g\,kg^{-1}$ dw) was the highest values among the alternative biocides detected (Table 5). Irgarol 1051 was detected in the range of 0.03–3.2 $\mu g\,kg^{-1}$ dw. M1 of the Irgarol's degradation product was in the range from 0.03 to 4.9 $\mu g\,kg^{-1}$ dw. The kinds and levels of detected alternative biocides in sediment were different among sampling sites. The concentrations of Diuron were over 5 $\mu g\,kg^{-1}$ dw at industrial areas. Irgarol 1051 was found in the highest concentration at a fishing ground and the site of the Royal Thai Navy Base. The concentrations of alternative biocides in green mussels are also measured. Although Sea Nine 211, Diuron, Irgarol 1051 and M1 were detected, the concentrations were lower than those in sediment.

Contamination by antifouling biocides in the coastal area of Malaysia

Harino et al. (2009b) reported the concentrations of BTs in sediment from the coastal water of Peninsular Malaysia along the Strait of Malacca of Malaysia (Table 4). TBT concentrations in Johor Strait were higher than those in other sites of Peninsular Malaysia, while the concentrations of PTs in Johor Strait were similar to those in the other sites. Furthermore, TBT in mussel samples from Peninsular Malaysia along the Strait of Malacca was detected in the range of 8–32 $\mu g\,kg^{-1}$ ww and the maximum value of TBT detected in the mussel samples was higher than TARL. TPTs were not detected in mussel samples along the Strait of Malacca.

The concentrations of Diuron and Irgarol 1051 in sediment from the study area were in the range of <0.04–4.8 and <0.04–14 $\mu g\,kg^{-1}$ dw, respectively. Sea Nine 211 and Dichlofluanid in sediment from the most sampling sites were not detected or near the detection limits. The higher concentration of alternative compounds was observed in southern part of Peninsular Malaysia; the distribution pattern is similar but the level is lower than those of OTs. Thus the contamination by OTs was found to be more serious problem than that by alternative compounds.

Contamination by antifouling biocides in the coastal area of Vietnam

Concentrations of MBT, DBT and TBT in sediments from Vietnam ranged from <0.1 to 11, from 0.6 to 4.6 and from 0.9 to 28 $\mu g\,kg^{-1}$ dw, respectively (Table 4) (Midorikawa et al. 2004). Concentrations of MPT, DPT and TPT in sediments from all sampling sites were in the range of 2.2–5.8, 0.1–3.6 and 0.1–0.4 $\mu g\,kg^{-1}$ dw, respectively. TBT in the sediment was highest at the trading port with many small vessels at a zone of poor flushing. Subsequently, the concentrations of TBT in sediment were high in the stations where are industrial areas with big international trading port. Concentrations of MBT, DBT and TBT in clam from all sites were in the range of 0.1–44, 0.5–10 and 1.4–56 $\mu g\,kg^{-1}$ ww, respectively, and the maximum concentration of TBT in clam was the values near the TARL. The concentration of TPT in clams was in the range of <0.1–3.1 $\mu g\,kg^{-1}$ ww and the concentrations of TPT in clams are lower than the value of TARL.

The concentrations of alternative biocides in the sediment samples from the coastal areas of northern and central Vietnam were measured (Table 5) (Harino et al. 2006b). Sea-Nine 211, Dichlofluanid, Duiron, Irgarol 1051 and Pyrithiones in sediment were detected. However, the detection frequencies of Dichlofluanid, M1 and Pyrithiones were low, ranging from 11–56%. The concentrations of Sea-Nine 211, Diuron and Dichlofluanid were higher in sediment from international trading ports with poor flushing of water and higher concentrations of Irgarol 1051 have been observed in fishing ports. Pyrithiones was detected in northern Vietnam.

The alternative biocides were under the detection limit in clams. These values imply a low bioconcentration of alternative biocide.

Comparison of concentration among regions in Southeast Asia

The concentrations of OTs in sediment were compared among Malaysia, Thailand and Vietnam by Harino et al. (2008c). The higher concentration and the wide variations of TBT and TPT in sediment from Malaysia and Thailand show that the more amounts of TBT have been used in coastal waters in these countries. The concentrations of alternative compounds in sediment were different among the countries. The higher concentrations were observed in Vietnam for Sea nine 211, in Thailand for Diuron, in Malaysia for Irgarol 1051. Even more noteworthy is the detection of pyrithiones in Vietnam, because it is considered that pyrithiones, which is unstable compounds, is undetectable in aquatic environment in theoretical sense.

Future study

Higher concentrations of TBT have been persisted in sediment in most countries. Furthermore, alternative biocides have been detected in Japan and Southeast Asia. Hereafter, it is forecasted that economic growth in developing countries will be in a high pace and marine pollution by antifouling biocides will expand. Therefore, further study is needed to monitor the antifouling biocides continuously and evaluate the risk of these compounds for aquatic organisms and, in addition to these researches, it is important to exchange the information for environmental problems between Japan and Southeast Asian countries through international cooperative research plan.

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