

Antifouling biocides contamination in sediment of coastal waters from Japan

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Abstract—The contaminations by antifouling biocide in sediment from four coastal waters (the Port of Osaka, Maizuru Bay, Otsuchi Bay and Tanabe Bay) were surveyed. Highest concentrations of tributyltin (TBT) and triphenyltin (TPT) were found in Tanabe Bay. Furthermore, the higher percentages of TBT for total butyltin (BT) and TPT for total phenyltin (PT) in this area were also observed in this bay, suggesting that a lot of organotin (OT) compound has been used for a long time.

The concentrations of "Sea Nine 211", "Diuron", "Dichlofluanid", "Irgarol 1051" and "M1" in four coastal waters of Japan were in the range of "0.10–12 $\mu\text{g kg}^{-1}\text{ dw}$ ", "0.76–120 $\mu\text{g kg}^{-1}\text{ dw}$ ", "0.1–1.0 $\mu\text{g kg}^{-1}\text{ dw}$ ", "<0.08–4.7 $\mu\text{g kg}^{-1}\text{ dw}$ " and "<0.18–1.3 $\mu\text{g kg}^{-1}\text{ dw}$ ", respectively. To find the characteristic of alternative biocides in four coastal waters, the ratios of Diuron for Irgarol 1051 were calculated. The ratio of Diuron was high in the Port of Osaka (international trading Port) and the ratio of Diuron was low in Maizuru Bay and Otsuchi Bay (fishing Ports). Assessment of alternative biocides depended on their application in respective study area.

Most alternative biocides cannot inhibit aquatic animals because most alternative biocides are chemical substances used as herbicides. To resolve this issue, alternative biocides containing copper oxide are found effective for animals. The contamination by copper was therefore surveyed in Otsuchi Bay and Maizuru Bay. Higher concentration of copper around shipyard in Otsuchi Bay suggests the copper contamination by antifouling paints.

Key words: butyltin, phenyltin, alternative biocides, copper, sediment

Introduction

Organotin (OT) compounds have been utilized as active biocides in antifouling paints since the early 1960s. Organotin compounds released into the water column from coatings applied to boat hulls caused deleterious effects such as endocrine disruptor for non-target marine organisms (Laughlin and Linden 1985, Bryan and Gibbs 1991), and 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) species 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. 1998).

In 2001, the International Maritime Organization (IMO) has adopted the International Convention on the Control of Harmful Antifouling Systems (AFS Convention), which prohibits the use of organotins (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.

After release of these antifouling biocides from the ship hulls and equipment such as fishing nets etc. into the aquatic environment, these chemicals are distributed in water, sediment, and aquatic organisms. The coastal waters of European countries and the USA are already polluted by alternative biocides (Gough et al. 1994, Toth et al. 1996, Gardinali et al. 2002, Bowman et al. 2003). In this paper, the concentrations and distribution of antifouling biocides in sediment from the

representative coastal area of Japan are discussed.

Materials and Method

Sampling description

Four sites of the Port of Osaka, Maizuru Bay, Otsuchi Bay and Tanabe Bay were selected as sampling sites of coastal waters from Japan (Fig. 1, Table 1). The Port of Osaka is an international trading port where is used every year by approximately 80,000 ships. There are many factories, marina, ferry terminal, small shipyard and mooring zones in the Port of Osaka. Maizuru Bay which faced the Japan Sea, has an average depth of 20 meters and is very calm. The water exchange in this bay is not good, because of shallow entrance (700 meters wide) and extremely small tidal variation (no more than 30 cm). This bay has been flourished as a military port for a long time and at the present day, fishery, battery, shipping and travel industries are carried out in this bay. Otsuchi Bay is comparatively small bay whose area is 20.2 km². There are many fishing ports and several scallop farms in this bay. The area of Tanabe Bay is 17.95 km². The main industries in this bay are fishery and aquaculture. Furthermore, climate is warm and many aquatic organisms live in this bay, because of the effect by Black current. After sediment samples from four coastal areas were collected by Eckman-Birge grab sampler, they were stored at -20 °C until analysis.

Chemical analysis

Organotin compounds

The method used to determine the OTs in sediment samples was based on that of Midorikawa et al. (2004) with some modifications. A hundred μL of mixed acetone solution containing $1 \mu\text{g mL}^{-1}$ each of monobutyltin trichloride (MBTCl₃)-d₉, dibutyltin dichloride (DBTCl₂)-d₁₈, tributyltin monochloride (TBTCl)-d₂₇, monophenyltin trichloride (MPTCl₃)-d₅, diphenyltin dichloride (DPTCl₂)-d₁₀ and triphenyltin monochloride (TPTCl)-d₁₅ as a surrogate standard was added to a centrifuge tube containing 1 g of sediment. The analytes were extracted by shaking for 10 min with 10 mL of 1 M HCl-methanol/ethyl acetate (1/1). After centrifugation, the supernatant was transferred to a flask. The residue was then extracted and centrifuged again in the same way. After centrifugation, the combined supernatants and 30 mL of saturated NaCl solution were transferred to a separatory funnel. The analytes were extracted twice with 15 mL of ethyl acetate/hexane (3/2) solution and the organic layer was combined. Fifty mL of hexane was mixed into the organic layer and left to stand for 20 min. After removal of the aqueous layer, the organic layer was dried with anhydrous Na₂SO₄

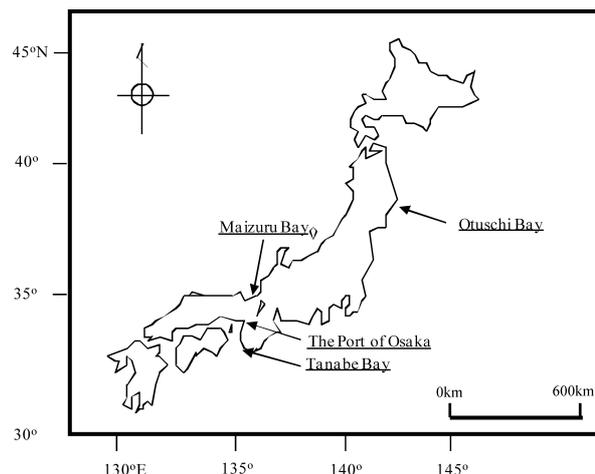


Fig. 1 Sampling sites of sediment used in the present study.

Table 1. Characters of sampling sites of sediment from Japan.

Locations	Years	Water depth	Characterization
The Port of Osaka	2004	10 m	International trading port
Otsuchi Bay	2005	77 m	Fishing port
Tanabe Bay	2005–2006	28 m	Fishing port, Aqua culture
Maizuru Bay	2007	30 m	Fishing port, Military port

and concentrated up to trace level. The analytes were diluted with 5 mL of ethanol, 5 mL of acetic acid-sodium acetate buffer (pH5.0) and 10 mL of distilled water and were then ethylated by shaking with 1 mL of 5% NaBEt₄ for 30 min. The solution containing ethylated OTs was saponified with 10 mL of 1M KOH-ethanol solution by shaking for 1 h. Forty mL of distilled water and 20 mL of hexane were added to the solution and the mixture was shaken for 10 min. The ethylated OT residue in the aqueous layer was extracted again by shaking for 10 min with 20 mL of hexane. The combined organic layers were dried with anhydrous Na₂SO₄. After being concentrated up to 1 mL, the solution was cleaned by a florisil Sep-Pak column (Waters Association Co. Ltd.). The analytes were eluted with 10 mL of 5% diethyl ether/hexane. All eluting solvent was collected in a bottom flask. The solution was concentrated up to 0.5 mL after the addition of 100 μL of mixed acetone solution containing $1 \mu\text{g mL}^{-1}$ each of tetrabutyltin (TeBT)-d₃₆ and tetraphenyltin (TePT)-d₂₀ as an internal standard. The final solution was concentrated up to 0.5 mL.

A Hewlett-Packard 6890 series gas chromatograph equipped with a mass spectrometer (5973 N) was used for analysis of the OTs. The separation was carried out in a capillary column coated with 5% phenyl methyl silicone (J&W Scientific Co., 30 m length×0.25 mm i.d., 0.25 μm film thickness). The column temperature was held at 60 °C

Table 2. Recovery rates of antifouling biocides in sediment.

Amounts (g)	Amount Spiked (μg)	Recovery rates /%					
		MBT	DBT	TBT	MPT	DPT	TPT
5	0.1	110 (10)	102 (8)	105 (8)	115 (9)	98 (10)	100 (6)
5	0.1	Sea-Nine	211 Diuron	Dichlofluanid	Irgarol 1051	M1	Pyrithiones
		85 (10)	95 (9)	75 (10)	95 (8)	78 (8)	80 (15)

Parenthesis shows relative standard deviation.

for the first 2 min, then increased to 130 °C at 20 °C min⁻¹, to 210 °C at 10 °C min⁻¹, to 260 °C at 5 °C min⁻¹ and to 300 °C at 10 °C min⁻¹. Finally, the column temperature was held at 300 °C for 2 min. The interface temperature, ion source temperature and ion energy were 280 °C, 230 °C and 70 eV, respectively. Selected ion monitoring was operated under this program. The monitoring ions of 235 (233) for MBT, 261 (263) for DBT, 263 (261) for TBT, 253 (255) for MPT, 303 (301) for DPT and 351 (349) for TPT were used to quantify the concentrations of OTs, respectively. The parentheses show the qualifier ions. One μL of the sample was injected with splitless injection. The concentrations of OTs in this study are expressed as Sn⁴⁺.

When 0.1 μg of OTs were spiked to 5 g of sediments, the recoveries of the OTs in sediment were in the range of 98–115% and the relative standard deviations (RSDs) of the OTs were in the range of 6–10% (Table 2). The detection limits were calculated from a signal-to-noise ratio of 3. The OT's detection limits were 0.1 $\mu\text{g kg}^{-1}$ dry weight (dw) for the sediment sample.

Alternative compounds

The method used for the determination of alternative compounds in sediment was based on that of Harino et al. (2005) with some modification. In the centrifuge tube, 5 g of wet sediment were placed together with 10 mL of acetonitrile. The mixture was shaken for 10 min in a mechanical shaker. After removal of the supernatant, the analytes were re-extracted with 10 mL acetonitrile for 10 min and the mixture was then centrifuged. The combined supernatants were concentrated by a rotary evaporator up to 5 mL and 45 mL of distilled water was added to them. The analytes were extracted three times with 10 mL of dichloromethane. The organic layer was dried by anhydrous Na₂SO₄. After 10 mL of methanol and 100 μL of atrazine-¹³C₃ (1 mg L⁻¹) were added to the organic layer, the organic layer was concentrated up to 2 mL by rotary evaporator. The analytes were determined by LC/MS-MS.

Liquid chromatograph was performed on an HPLC apparatus equipped with an Agilent model 1100 series (Agilent, Yokogawa Analytical Systems, Tokyo, Japan). The separation was carried out on a narrow bore C₁₈ silica column (2.1 × 50 mm, 5 μm , TOSOH COOPARATION). The mobile phase was methanol-water run over a gradient (50% of methanol linear to 100% of methanol for 20 min and held for 10 min). The injection volume was 10 μL .

Electrospray mass spectrometer (ESI-MS-MS) analyses were carried out using a PE-Sciex API2000 (Sciex, Applied Biosystems Japan). Ionization of the analytes was achieved by electrospray in the positive ion mode. All the interface parameters were optimized by infusion of a standard solution (1 mg L⁻¹) of the analytes at the flow rate of 20 mL min⁻¹. The final electrospray conditions were as follows: nitrogen curtain gas, 40 L min⁻¹, ion spray voltage, 4800 V, ion source gas 1, 40 $\mu\text{L min}^{-1}$, gas 2, 70 $\mu\text{L min}^{-1}$, collision gas 4 $\mu\text{L min}^{-1}$. LC/MS-MS acquisition was performed in the multiple reaction monitoring (MRM) mode and precursor ion/product ion of Sea-Nine 211, Diuron, Dichlofluanid, Irgarol 1051, M1 and Pyrithiones were 282/170 (43), 233/46 (160), 333/224 (123), 254/198 (83), 214/158 (43) and 316/190 (189) respectively. The parentheses show the qualifier ion.

When 0.1 μg of each alternative biocide was spiked to 5 g of sediments, the recoveries of the each alternative biocide in sediment samples were in the ranges of 75–95%, and their RSDs were in the range of 8–15% (Table 2). The detection limits of Sea-Nine 211, Diuron, dichlofluanid, Irgarol 1051, M1 and Pyrithiones were 0.04, 0.08, 0.1, 0.08 and 0.18 and 8 $\mu\text{g kg}^{-1}$ dw for the sediment samples respectively.

Copper analysis

The method was based on that of Ministry of the Environment (1988) with some modification. Three g of sediment were heated at 180 °C with 10 mL of concentrated nitric acid and 4 mL of concentrated perchloric acid for 3 hours. Sediment samples were re-heated with 3 mL of hydrogen peroxide for 30 min. Copper was determined directly measured by flame atomic absorption spectrophotometer.

Results and Discussion

The concentration of organotin compounds

The concentrations of TBT in sediment from the Port of Osaka, Maizuru Bay, Otsuchi Bay and Tanabe Bay are shown in Table 3. TBT concentrations were high in the order of Tanabe Bay (means 580 $\mu\text{g kg}^{-1}$ dw), The Port of Osaka (means 58 $\mu\text{g kg}^{-1}$ dw), Otsuchi Bay (means 28 $\mu\text{g kg}^{-1}$ dw) and Maizuru Bay (means 3.4 $\mu\text{g kg}^{-1}$ dw). It is reported that means of TBT concentrations in sediment around the coastal waters from Japan ranged of 4–183 $\mu\text{g kg}^{-1}$ dw (Harino et al. 2008). Although the sediment in Tanabe Bay was contami-

nated heavily by TBT, TBTs in the other areas were within the range of previous reported values in Japan. Furthermore, TBT and its degradation products (DBT and MBT) were also higher in Tanabe Bay than those in other coastal waters of Japan (Table 3). The concentrations of sediment show the integration of the load of OTs, because it is reported that TBT is not degraded in sediment (Maguire and Tkacz 1985, Dowson et al. 1993). Therefore, higher concentrations of TBT in Tanabe Bay show that a lot of amount of TBT have been used in Tanabe Bay for a long time.

The concentrations of TBT in sediment were compared with those in Vietnam (Midorikawa et al. 2004), Thailand (Harino et al. 2006a), Malaysia (Harino et al. 2009), India (Jadhav et al. 2009), Taiwan (Meng et al. 2009) and China (Cao et al. 2009) where are non-regulated Asian countries for OTs (Table 3). Although the highest concentration of BTs was detected in Tanabe Bay among four coastal waters from Japan, the concentrations of BTs in Tanabe Bay were within the range of the other Asian countries.

TPT were detected in the ranges of <0.1 – $270 \mu\text{g kg}^{-1}$ dw (means $26 \mu\text{g kg}^{-1}$ dw) for the Port of Osaka, 0.2 – $19 \mu\text{g kg}^{-1}$ dw (means $7.5 \mu\text{g kg}^{-1}$ dw) for Maizuru Bay, <0.1 – 88

$\mu\text{g kg}^{-1}$ dw (means $11 \mu\text{g kg}^{-1}$ dw) for Otsuchi Bay, 0.9 – $6,900 \mu\text{g kg}^{-1}$ dw (means $1,100 \mu\text{g kg}^{-1}$ dw) for Tanabe Bay (Table 3). TPT concentration in Tanabe Bay was higher in comparison to the other areas as well as TBT, and TPT was dominant species in Tanabe Bay (Table 3). It is reported that TPT in sediment from India were detected in the ranges of ND (not detected)– $17 \mu\text{g kg}^{-1}$ dw, which is due to the use of TPT in shipbuilding factory (Jadhav et al. 2009). Meng et al. (2009) reported that TPT in sediments from Taiwan were detected in the ranges of ND– $1,811 \mu\text{g kg}^{-1}$ dw and the origin of TPT in Taiwan is the use of agriculture in addition to the antifouling paint. Comprehensively, TPT concentrations in sediment from Japan were high in comparison with the other Asian countries. Furthermore, the TPT concentrations in Tanabe Bay were higher than TBT concentrations. Eguchi et al. (2009) reported that TPT concentrations were higher than TBT near sampling site where was used as the timber-yard, suggesting the use of TPT as a pesticide. Results also suggest that a lot of TPT have been used as an antifouling paint and a pesticide in Tanabe Bay of Japan.

In Norway, a guideline for classification of environmental quality in ports and coastal waters is enacted (Norwegian

Table 3. The concentrations of antifouling biocides in Asian countries ($\mu\text{g kg}^{-1}$ dw).

1) Midorikawa et al. 2004, 2) Harino et al. 2006b, 3) Harino et al. 2006a, 4) Harino et al. 2009, 5) Jadhav et al. 2009, 6) Meng et al. 2009, 7) Cao et al. 2009

	MBT	DBT	TBT	MPT	DPT	TPT	SeaNine 211	Diuron	dichlo fluanid	Irgarol 1051	M1	Pynithione
The port of Osaka	2.2–590 (93)	0.8–720 (100)	0.6–240 (58)	0–670 (62)	0.1–520 (64)	<0.1 –270 (26)	<0.04 –110 (12)	0.4–900 (120)	<0.1 –0.8 (0.1)	0.5–23.3 (4.7)	<0.18 –8.2 (1.3)	<8 (<8)
Maizuru Bay	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)	<0.04 –7.2 (0.9)	<0.08 –12 (5.9)	0.1 (0.1)	<0.08 –9.8 (3.7)	<0.18 (<0.18)	<8 (<8)
Otsuchi Bay	0.3–120 (38)	1.5–80 (15)	<0.1 –200 (28)	<0.1 –190 (43)	<0.1 –28 (4.8)	<0.1 –88 (11)	<0.04 –0.3 (0.10)	0.1–18 (3.2)	0.1–14 (1.0)	<0.08 –21 (1.7)	<0.18 –0.50 (<0.18)	<8 –22 (<8)
Tanebe Bay	0.2–1900 (380)	2.3–980 (220)	2.6–4,600 (580)	0–290 (91)	0.7–5,500 (680)	0.9–6,900 (1100)	<0.04 –0.33 (0.11)	0.08–2.1 (0.76)	0.1 (0.1)	<0.08 (<0.08)	<0.18 (<0.18)	<8 (<8)
Vietnam ¹⁾	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)	0.1–1.3 (0.50)	0.1–3.0 (1.2)	<0.1 –13.3 (2.8)	<0.08 –4.0 (0.80)	<0.18 –0.40 (0.20)	<8 –422 (42)
Thailand ²⁾	1.0–290 (56)	0.7–370 (57)	1.6–1,200 (160)	0.3–9.5 (2.0)	0.3–5.6 (1.1)	0.3–29 (7.0)	<0.04 –0.1 (<0.04)	0.12–5.4 (3.5)	<0.1 –13.3 (2.8)	<0.08 –3.2 (0.50)	<0.18 –4.9 (0.60)	<8 (<8)
Malaysia ³⁾	4.1–542 (130)	1.1–230 (58)	0.7–490 (97)	0–120 (40)	0.4–29 (9.9)	0.1–34 (11)	<0.04 –1.7 (0.10)	0.08–4.8 (0.7)	<0.1 (<0.1)	<0.08 –14 (1.6)	<0.18 (<0.18)	<8 (<8)
India ⁴⁾	2.0–2,238 (–)	1.8–1,030 (–)	6.5–4,353 (–)	ND–13 (–)	ND–17 (–)	ND–17 (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)
Taiwan ⁵⁾	– (–)	– (–)	1.0–20,220 (–)	– (–)	– (–)	ND–1811 (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)
China ⁶⁾	2.0–2,238 (–)	1.8–1,030 (–)	6.5–4,353 (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)
Spain ⁷⁾	5.0–1,130 (–)	67–3,519 (–)	98–7,673 (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)

Parenthesis shows average, ND: not detected

pollution control authority, 2007). In this guideline, five contamination levels (Background, Good, Moderate, Bad and Very bad) were classified from the content of metals and organic matter in sediments. Based on this guideline, TBT concentrations in Japan can be classified as very bad level, which suggests severe acute toxicity level.

The concentration of alternative compounds

The concentrations of alternative biocides are shown in Table 3. Mean concentrations of Sea Nine 211 in the coastal areas from Japan were in the range of $0.10\text{--}12\ \mu\text{g kg}^{-1}\text{ dw}$. These values are similar concentrations to Vietnam, Thailand and Malaysia (Harino et al. 2006a, 2006b, 2009). Sea Nine 211 was not detected in sediment from Southampton, England (Thomas et al. 2002). The means of Diuron in four coastal waters of Japan were in the range of $0.76\text{--}120\ \mu\text{g kg}^{-1}\text{ dw}$. Diuron was detected in the range of $0.7\text{--}3.5\ \text{mg kg}^{-1}\text{ dw}$ in sediment from Vietnam, Thailand and Malaysia. The concentrations of Diuron in Japan were higher than those in Southeast Asia. In guideline of Norway, contamination levels of Diuron in sediment were clarified. Diuron was the levels between bad and very bad. In spite of trace level ($0.1\text{--}1.0\ \mu\text{g kg}^{-1}\text{ dw}$), Dichlorofluanid was detected in coastal areas from Japan. Voulvoulis et al. (2000) reported that Dichlorofluanid was in the range of $<4.9\text{--}688\ \mu\text{g kg}^{-1}\text{ dw}$ in Blackwater estuary, England. However Thomas et al. (2002) suggested the possibility of no detection of Dichlorofluanid in sediment, because the half lives of Dichlorofluanid in water is 0.8 day. The detection of Dichlorofluanid in sediment is considered to be derived from the paint chips (Paints that removed from ship hull), which contain certain amount of Dichlorofluanid, and deposited into the sediment. The means of Irgarol 1051 and M1 in four coastal waters of Japan were in the range of $<0.08\text{--}4.7\ \mu\text{g kg}^{-1}\text{ dw}$ and $<0.18\text{--}1.3\ \mu\text{g kg}^{-1}\text{ dw}$, respectively. Irgarol 1051 was detected in the range of $0.5\text{--}1.6\ \mu\text{g kg}^{-1}\text{ dw}$ in sediment from Vietnam, Thailand and Malaysia. The concentrations of Irgarol 1051 in Japan were similar concentrations to those in Southeast Asia. In guideline of Norway, Irgarol 1051 in this study areas except for Tanabe Bay were the levels between bad and very bad. Irgarol 1051 was not detected in Tanabe Bay. Pyrithions was not detected in four coastal areas in Japan. Pyrithions was only detected in Vietnam. Turley et al. (2000) reported rapid disappearance of Pyrithiones from water. The detection of Pyrithione may be due to the entrainment of pyrithione enriched paint chips derived from ship hulls.

The detection frequencies of Diuron and Irgarol 1051 in sediment from Japan are higher than the other alternative biocides. Therefore, in order to find the characteristic of alternative biocides contaminations in various coastal areas, the ratios of Diuron for Irgarol 1051 were calculated (Fig. 2). The ratio of Diuron was high in the Port of Osaka which is the international trading port. On the other hand, the ratio of

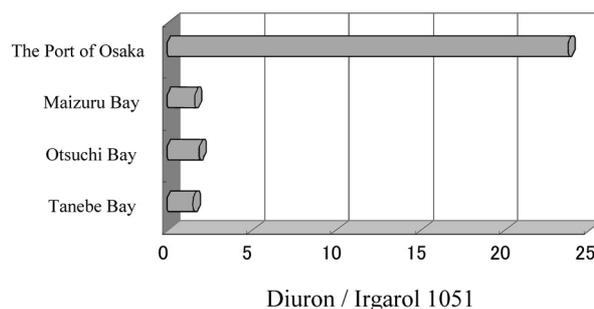


Fig. 2 The ratio of Diuron for Irgarol 1051 in sediment.

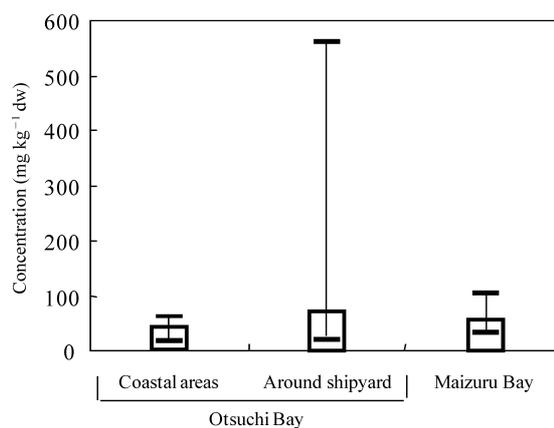


Fig. 3 The concentrations of copper in sediment from Otsuchi Bay and Maizuru Bay.

Irgarol 1051 was high in fishery harbour. Liu et al. (1999) reported that Irgarol 1051 was found more frequently in fishery harbours than in marines and trading ports and fishery harbors is a significant source of contamination of antifouling biocides. Our result supports the paper by Liu et al. (1999). There are a lot of source of antifouling biocide contaminations such as small ship, fishing net etc. in fishing port. Further study is needed to survey the contributing rate of antifouling biocide to aquatic environment from fishing equipment and fishing boat.

The concentration of copper in sediment

Alternative biocides have been used with copper oxide, because most of alternative biocide is not effective for animal. Therefore there is fear that the coastal area is contaminated by copper. The concentrations of copper were surveyed in sediment from Otsuchi Bay (Fig. 3). Copper was detected at the range of $20.8\text{--}561\ \text{mg kg}^{-1}\text{ dw}$ (means $71\ \text{mg kg}^{-1}\text{ dw}$) around shipyard and was ranged of $18.4\text{--}63\ \text{mg kg}^{-1}\text{ dw}$ ($45\ \text{mg kg}^{-1}\text{ dw}$) in coastal area except for shipyard. Higher concentration of copper around shipyard suggests the elution of copper on the ship hull. Harino et al. (2007) reported that copper has a higher correlation with TBT, TPT and Diuron, indicating that these compounds are used with copper as an antifouling biocide on ships. The concentrations of copper in

Maizuru Bay were similar to those in Otsuchi Bay except around shipyard (Fig. 3).

The concentrations of copper were compared to the value in the guideline of Norway. The concentrations of copper in Otsuchi Bay except for near the shipyard and Maizuru Bay were the levels between moderate and bad. However, area around the shipyard from Otsuchi Bay can be classified as very bad polluted with copper.

Conclusion

Although about twenty years have passed after regulation in Japan, TBT and TPT have still detected in sediment from coastal water of Japan. Furthermore, alternative biocides were also detected in sediment from Japan. Therefore, it is necessary to pay attention to the change of antifouling biocides concentrations in future. Further studies are to continue the monitoring program of antifouling biocides and to clarify the effect of alternative biocides on aquatic organisms.

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