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Concentration of Organotin and Booster Biocides in Sediments of Seagrass Area from Sungai Pulai Estuary, South of Johor, Malaysia

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Received: 2 January 2019; Accepted: 25 January 2019; Published: 25 February 2019

Abstract: Antifouling compounds are widely used in paints applied on ship hulls to prevent attachment of fouling organisms. However, a certain amount of these chemicals could leach from the painted surface, enter seawater, and pose deleterious effects on various marine biotas. The present study aimed to determine the concentration of organotin (OT) compounds and booster biocides in sediments collected from the seagrass area of Sungai Pulai estuary, Malaysia. The sediment samples were collected from three points on the seagrass bed, brought back to the laboratory, extracted using standard extraction procedure, and the analytes were analysed using gas chromatography-mass spectrometry (GC-MS) method. The results showed that tributyltin (TBT) concentrations in sediments were within the range of 8.1 ± 0.4 to 10.6 ± 0.5 μg/kg, whereas the values of triphenyltin (TPT) were between 17.1 ± 0.9 and 19.4 ± 1.0 μg/kg. The range of concentration of booster biocides, namely diuron, dichlofluanid chlorothalonil, Irgarol 1051, M1, and Sea-Nine 211, were from <0.1 to 22.9 ± 1.1, 48.7 ± 2.4 to 800 ± 40, <0.1 to 6.2 ± 0.3, <0.1 to 1.4 ± 0.1, 44 ± 2.2 to 877 ± 44, and 9.1 ± 0.5 to 170 ± 8.5 μg/kg, respectively. The concentration of organotin was much lower than the previous study conducted in southern Johor. Meanwhile, the increased concentration of booster biocides proves the use of these compounds as antifouling paints in shipping systems nowadays.

Keywords: organotin; booster biocides; antifouling paint; shipping; seagrass; sediment

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1. Introduction

The organisms that settle and grow on the external of submerged or semi-submerged object are known as marine biofouling [1]. The initial colonisation of organisms occurs when the slime layer begins to develop in submerged areas, which gains the growth of microscopic (e.g., bacteria and algae) and calcareous (e.g., mussels and barnacles) organisms [2]. The colonisation of organisms is a serious problem in the shipping industry. The organisms on ship hulls increase friction, which reduces the ship speed and increases the fuel consumption in order to maintain the ship speed [3]. The friction of ship hull will increase about 80% with only 1 mm thick of algal slime and decrease the speed about 15% [4]. Therefore, organotin (OT) compounds are used in ship paints to maintain the effectiveness of ship functionality in the long term [5] by avoiding the attachment of marine organisms to the hulls.

Since the early 1960s, OT compounds especially tributyltin (TBT) and triphenyltin (TPT) are commonly used as the ingredient in antifouling paints. However, these compounds have the potential to leach into marinas, followed by wide spreads of toxicants resulting in high concentration level of contamination in the environment. OT compounds are poorly biodegradable and have the potential to remain long in the aquatic environment, which can cause deleterious effects towards marine organisms. The effects of TBT in marine environment include acute toxicity [6–10], bioaccumulation in the organism [11–17], imposex [18–21] followed by a decrease in reproductive viability of marine organisms. In October 2001, the International Maritime Organization adopted the International Convention on the control of Harmful Anti-fouling System (AFS Convention) that banned the use of OT compounds as a substance in ship antifouling paints starting from 2003. However, OT compounds are still used in several areas, especially in the developing countries, including Malaysia [22].

Since the ban of OT compounds, a number of OT-free antifouling paints have been manufactured. Booster biocides are highly degradable and require less time to remain in the aquatic environment [23]. Commercial OT-free antifouling paints that are widely used nowadays include chlorothalonil, dichlofluanid, diuron, Irgarol 1051, Sea-Nine 211, TCMS pyridine, TCMTB, zinc pyrithione, and zineb [24]. However, these compounds also cause problems in the marine ecosystem. At a very low concentration, the photosynthesis of plants can be affected in the value of parts per trillion (ng/L). Irgarol 1051 and Diuron act as herbicides that inhibit photosynthesis by blocking the electron transfer in photosystem II [25]. This situation interrupts the photosynthetic electron transport chain in photosynthesis and thus reducing the ability of the plant to convert light energy into chemical energy (ATP and reluctant potential). Moreover, the accumulation of booster biocides in aquatic life can reduce the germination and growth of non-target organisms such as algae, *Hormosira banksii* [26], and the seagrass, *Zostera marina* [27]. If the situation continues in the long term, there is a potential for disturbance of food-web cycle when the producers are under threat. Another major concern about booster biocides is the accumulation of compounds from the lower trophic level that is then transferred to the higher trophic level, which involves organisms as the important sources of food for human [28]. High concentration of booster biocides detected in marine food is risky for human health. In Malaysia, there is a lack of data on the concentration of OT and booster biocides in sediment for further reference. Due to this fact, the study was conducted to investigate the degree of concentration of OT and booster biocides in the sediments collected from the seagrass area of Sungai Pulai estuary in southern Johor, Malaysia. The present paper reports the recent contamination and distribution of butyltins (BTs) and penyltins (PTs) compound in marine environment including their breakdown products.

2. Materials and Methods

2.1. Study Area

The study was carried out in the seagrass area of Sungai Pulai estuary, located in southern Johor, (latitude N 01°20.137′, E 103°35.158′) as illustrated in Figure A1. The seagrass area varies in size from 120 to 1000 m in length and 50 to 120 m in width [29]. Seagrass roots and rhizomes stabilize the sediment on the seagrass bed, which reduces soil erosion. This unique area becomes a protective shelter for diverse species of marine organisms from all trophic levels [30]. However, human development activities, mainly shipping activities near the study area, release more OT and booster biocides into the environment, including sediments. Other human activities around the study site include land reclamation for port facilities and palm oil plantation, which have the possibility to release herbicides into the coastal area.

2.2. Sample Collection

Surface sediment samples were collected in triplicate by using a scoop at three different points on the seagrass bed. All the sediments collected were stored in clean polyethylene bags, kept in a cooler box with ice, transported to the laboratory and immediately kept in a deep freezer at −20 °C prior to the next analytical procedures.

2.3. Chemical Analysis

2.3.1. Organotin

Target compounds were extracted from sediment samples according to the method described by Harino et al. [31] with some modification. About 1 g of sediment in a centrifuge tube was homogenized with 10 mL of hydrochloric acid (HCl)-methanol/ethyl acetate (1:1) (analytical reagent, Kanto Chemical Co. Inc., Japan) and 100 μL of surrogate standard solution monobutyltin-d_9 (MBT-d_9), tributyltin-d_{27} (TBT-d_{27}), diphenyltin-$_{10}$ (DPT-d_{10}), dibutyltyin-d_{18} (DBT-d_{18}), monophenyltin-d_5 (MPT-d_5), and triphenyltin-d_{15} (TPT-d_{15}). The mixture was shaken for 10 min. After shaking, the residue was again extracted with 10 mL of hydrochloric acid (HCl)-methanol/ethyl acetate (1:1). The combined supernatant was transferred into a separatory funnel containing 30 mL of 30% sodium chloride (NaCl) (assay $\geq$ 99.5%, Wako, Japan) aquatic solution. The analyte was extracted twice with 10 mL of ethyl acetate:hexane (3:2) (analytical reagent, Kanto Chemical Co. Inc., Japan) for 10 min. The combined organic layer was mixed into 50 mL of hexane (analytical reagent (96%)), Kanto Chemical Co. Inc., Japan) and left to stand for 30 min. Aqueous layer was removed and the organic layer was dried by adding anhydrous sodium sulphate (Na_2SO_4) (Kanto Chemical Co. Inc., Japan). The collected analyte was concentrated to 2 mL. The concentrated analyte was diluted with 3 mL of ethanol (analytical reagent (assay $\geq$ 99.5%), Wako, Japan), transferred to a separatory funnel, and added with 1 mL of acetic acid-sodium acetate buffer solution (pH 5) (Wako, Japan), and 10 mL of distilled water, and subsequently ethylated by shaking with 1 mL of 2% sodium tetraethyl borate (Wako, Japan) for 30 min. The solution was saponificated with 10 mL of 1 M of potassium hydroxide (KOH)-ethanol solution (Wako, Japan) by shaking for another 1 h. Then, the solution was extracted twice with 50 mL of distilled water, 10 mL of hexane, and shaken for 10 min. Water layer was removed and the combined organic layer was dried with anhydrous Na_2SO_4. After being concentrated to 1 mL, the analyte was cleaned with Florisil SEP-PAK, followed by elution with 10 mL diethyl ether and hexane. The final solution was concentrated up to 1 mL with N_2 before 100 μL of internal standard was injected (TeBT-d_{36}, TePT-d_{20}, 1 mg/L in hexane).

2.3.2. Booster Biocides

The sediment samples for determination of booster biocides were extracted through liquid-liquid extraction as referred from the method by Harino et al. [31]. In a centrifuge tube, 1 g of sediment was added twice with 10 mL of acetone (analytical reagent (assay $\geq$ 37%), Sigma-Aldrich, USA) and shaken for 10 min, followed by centrifugation for another 10 min. The combined supernatant was added with 50 mL of distilled water, 0.5 g of celite (Wako, Japan), and 1 g of zinc acetate dehydrate (Wako, Japan), and allowed to stand for 30 min. The analyte was filtered with Whatman filter paper into a separatory funnel, added with 10 mL of dichloromethane (analytical reagent (99.5%)), Kanto Chemical Co. Inc., Japan) twice, and shaken for 10 min. The combined analyte was dried with anhydrous Na_2SO_4 (Kanto Chemical Co. Inc., Japan). The solution was added with 20 mL of hexane and evaporated to 2 mL. The analyte was injected with 100 μL of internal standard (atrazine-d_5) and adjusted to 1 mL with N_2.

2.4. Instrument Analysis

Gas chromatography model of Hewlett-Packard 6890 equipped with a mass spectrometry (5973N) (GC-MS), (Agilent; Wilmington, USA) was used to analyse OT and booster biocides. The separation was carried out in a capillary column coated with 5% phenyl methyl silicone (30 m length × 0.25 mm inner diameter × 0.25 μm film thickness). The column temperature was held at 60 °C for the first 2 min, then increased to 130 °C at 20 °C/min, to 210 °C at 10 °C/min, to 260 °C at 5 °C/min, to 300 °C at 10 °C/min, and held at 300 °C for 2 min. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The interface temperature, ion source temperature, and ion energy were 280 °C, 230 °C, and 70 eV, respectively. The selected monitoring ions used under this program to quantify the concentrations OTs included 235 for monobutyltin (MBT), 261 for dibutyltyin (DBT), 263 for tributyltin (TBT), 253 for monophenyltin (MPT), 303 for diphenyltin (DPT), and 351 for triphenyltin (TPT), respectively. Meanwhile, monitoring ions for booster biocides were 187 for diuron, 224 for dichlorofluanide, 266 chlorothalonil, 253 for Irgarol 1051, 213 for M1, and 169 for Sea-Nine 211. Splitless injection (1 µL) was employed and the injection temperature was 290 °C.

2.5. Degradation Index Calculation

OTs compound can be predicted either as 'old' or 'fresh' using butyltin degradation index (BDI) and phenyltin degradation index (PDI) [32]. The following equations were calculated based on the concentration ratios between two main degradation products (MBT and DBT, MPT and DPT) from the parent compound, by which it was assumed that the degradation rates between both compounds are similar [33]. BDI values higher than 1 indicate TBT or TPT input in sediment is 'old', whereas BDI values less than 1 show a 'fresh' input of TBT or TPT [34].

$$\mathrm{BDI} = \frac{[\mathrm{MBT}] + [\mathrm{DBT}]}{[\mathrm{TBT}]} \tag{1}$$

$$\mathrm{PDI} = \frac{[\mathrm{MPT}] + [\mathrm{DPT}]}{[\mathrm{TPT}]} \tag{2}$$

3. Results and Discussion

3.1. Concentration of Organotin Compounds in Sediments

OT concentrations in sediment are tabulated in Table 1 (Figure 1). Intensive marine activities in the Peninsular Malaysia release more OT concentration, mainly in the Straits of Malacca, including Penang and Johor [35]. Therefore, antifouling biocides are expected to be accumulated in this study area. The concentrations of MBT, DBT, and TBT in sediment ranged from 6.5 ± 0.3 to 12.2 ± 0.6, <0.1 to 6.1 ± 0.3, and 8.1 ± 0.4 to 10.6 ± 0.5 µg/kg, respectively. The BT compounds in the sediments represent the direct relationship that exists from the broadly marine transports and industrial materials of biocides such as large scale use of polyvinyl chloride (PVC) which contains mono- and diorganotin compounds as stabilizers [36]. A previous study showed higher concentrations of BTs in southern Johor with the range concentrations from 25 to 240, 20 to 190, and 41 to 230 µg/kg for MBT, DBT and TBT, respectively [19]. These were due to the poorly flushed water where the water exchange with the open sea and has limited tidal movement, as well as high shipping activities. Thus, it is predicted that BTs have been used in the past and persisted for years before the concentrations are declining nowadays. High temperature in Malaysia might help in accelerating the degradation of BT compounds [37]. Additionally, other significant factors for OT compounds that degrade in the environment is ultraviolet breakdown [38–40], and, biotic degradation process by which certain fungi and bacteria are able to break down the compound [41]. The presence of TBT level in sediments can be classified as light (TBT = 1.2–8.2 µg/kg) for Point 1 and moderate (TBT = 8.2–41 µg/kg) for Points 2 and 3 [41]. However, the total OT in sediments is much higher at Point 1. Point 1 is exposed to the open strait of the shipping channel that is possible to absorb OT compounds directly into the seagrass bed sediment.

Table A1 shows BTs concentrations in sediments from diverse locations around the world. The ability of sediments to accumulate the compounds varies geographically and geologically. The geological element is based on the physicochemical characteristics of sediment such as particle size and organic carbon content [42,43]. Generally, the concentrations of BTs in the sediments collected from this seagrass area are lower than those reported at other locations, such the studies conducted in the semi-closed Port of Gdynia [44], fishing ports along the Chinese coast [45], Southern Baltic coastal zone [46], Kaohsiung Harbour, Taiwan [47], and Korean Special Management Sea Areas [48]. The results are probably due to the prohibited use of OT as an ingredient in paints on ship hulls since 2008 and the compounds that degrade in sediments due to ecological and physical reactions [18]. Dredging and dumping process that frequently occurs across the seagrass bed develop the potential to change marine base, such as sediment shifting that release of OT compounds from sediments into the water column. Moreover, the occurrence of developing activities is possible to release more oxygen into waters which speed up the degradation process of OTs in aerobic condition rather than anaerobic [49,50].

Table 1. Concentration of organotin compounds in sediment collected from seagrass area of Sungai Pulai estuary (µg/kg).

Point	n	MBT	DBT	TBT	MPT	DPT	TPT
		Mean ± SD					
Point 1	3	6.5 ± 0.3	6.1 ± 0.3	8.1 ± 0.4	<0.1	89.1 ± 0.5	17.1 ± 0.9
Point 2	3	12.2 ± 0.6	<0.1	10.6 ± 0.5	<0.1	10.2 ± 0.5	19.4 ± 1.0
Point 3	3	7.4 ± 0.4	<0.1	10 ± 0.5	16 ± 0.8	9.3 ± 0.5	17.7 ± 0.9

SD: Standard deviation.

The concentrations of MPT, DPT, and TPT in sediments ranged from <0.1 to 16 ± 0.8, 9.3 ± 0.5 to 89 ± 0.5, and 17 ± 0.9 to 19.4 ± 1.0 µg/kg, respectively. These concentrations were much higher than BTs. High TPT occurred in marine sediments indicates considerable input and persistence. The concentration detected might be due to intensive palm oil plantation activities taking place around the location. TPT is a co-toxicant of TBT compound applied in antifouling paint and also widely used in pesticide formulations in agricultural activities [51]. The detectable values are within the range of previous study in the south of Peninsular Malaysia [22,37]. Meanwhile, the concentration of PTs in sediments was relatively lower than the studies conducted in Indonesian coastal waters [31], Gulf of Thailand, Thailand [52], and Otsuchi Bay, Japan [53]. Among PTs compound, TPT is the dominant species. TPT residues have the potential to degrade naturally in sediments before the residues are released into the water column. In the aquatic ecosystem, TPT compounds have low solubility rate. Therefore, they are able to adsorb onto suspended particulate matter (SPM), lead to TPT scavenging in sediments, and amounts of TPT, and its degradation products can be detected. TPT is mainly present in the upper 2–3 cm of the sedimentary column due to recent activities in aquatic systems [54].

The BDI and PDI values of organotin compound are recorded in Table 2. Sediments collected from Points 1 and 2 had BDI values >1, indicating no recent input and the TBT content in sediments was 'old'. Meanwhile, Point 3 had the BDI value of 0.74, indicating a 'fresh' input of TBT. For Point 1, the PDI value was >2, implying a rapid degradation of TPT, DPT, and MPT, and there was no new TPT input for this point. For Points 2 and 3, the PDI values were 0.53 and 0.52 respectively, indicating a 'fresh' input and low rate of TPT degradation. As the degradation products were detected to be higher than the parent compound, there was less TBT available in the sediments. The products of OT degradation are less toxic than the parent compound [55]. TBT compound in surface sediment has a long half-life ranging between 160 and 775 days before the compound produces other BT products: MBT and DBT. Both BT products are produced by aerobic biological process but with less oxygen condition, mainly in deeper sediments, the degradation becomes slower [56].

Table 2. BDI and PDI value for organotin compound.

Point	BDI	PDI
Point 1	1.56	5.20
Point 2	1.15	0.53

After the restriction of OT used in the painting system in 2008, the compounds were still contaminating various marine environment globally. OT compounds detected in Hong Kong marinas caused ecological risk to local rock shell population, where both imposex levels and tissue concentrations of OT did not decline since 2004 [57]. After being banned for 10 years in Jinhae Bay, South Korea from 2003 to 2010, a significant reduction of TBT concentration was detected in seawater and oysters but there was no significant change in sediments. Therefore, TBT concentration remained above the global environmental quality control [58]. BTs were still detected in surface sediments and hermit crabs after the international and Brazilian bans, with the range of 1.32 to 1746 ng Sn g^{-1} in biotas and 7 to 1304 ng Sn g^{-1} in sediments [59]. Otherwise, in Bizerta channel, northern Tunisia, the TBT levels recorded in the gastropod *Hexaplex trunculus* decreased over time and the compound was less frequent among BTs [60]. The ban of TBT also showed the decline of imposex frequency and concentration of TBT for rock shells in South Korea [61]. The implementation of international regulations might be effective enough to control the widespread of OT contamination in certain areas. However, actions from the local managements are also needed to overcome these unsolved problems in the future.

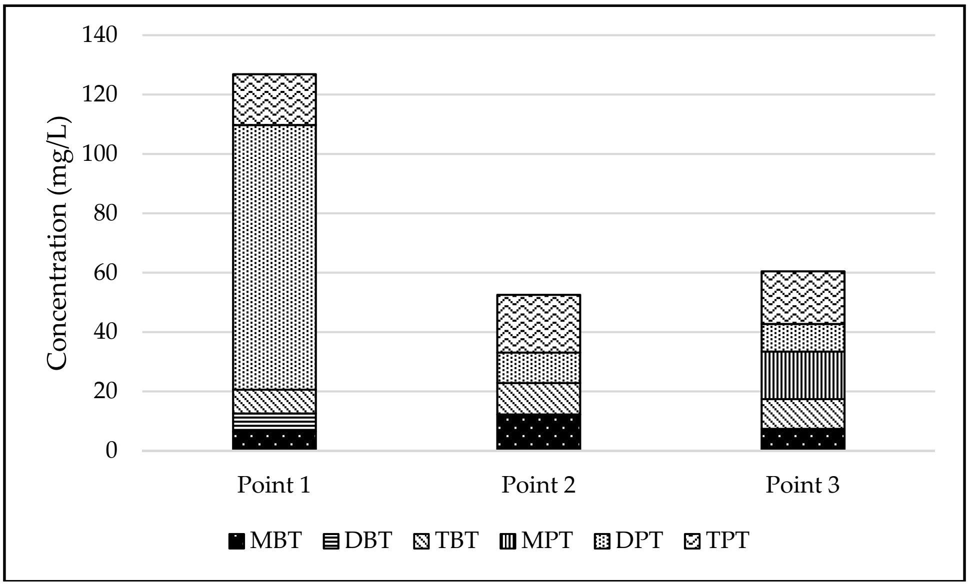

Figure 1. Concentration of OTs compound on seagrass bed of Sungai Pulai.

3.2. Distribution of Booster Biocides in Sediments

The replacement of OT compounds used in antifouling paints was carried out in this study, including diuron, dichlofluanid, chlorothalonil, Irgarol 1051, M1, and Sea-Nine 211 (Table 3) (Figure 2). The range of diuron concentration in sediments was <0.1 to 22.9 ± 1.1 µg/kg. The concentration was higher from a previous study reported in 2009 for the sediments from selected regions of Malaysian coastal areas [37], but in a similar range to a study reported in 2017 for the sediments obtained from Port Klang, Malaysia [62], with the values of <0.02 to 4.8 and 2.24 to 19.28 µg/kg, respectively. The concentration of sediments for the current study was also within the range for the concentration from a study in Panamanian marinas at <0.75 to 14.1 µg/kg [63]. Compared to the study in Korean coastal areas, the concentration for Malaysian marinas was much lower. The study reported the concentration of diuron in the range of 2.3 to 62.3 µg/kg in shipping and shipbuilding areas in South Korea [64] (Table A2). Another study showed that in Busan and Ulsan Bay, South Korea, the concentrations of diuron were from 6.89 to 29.9 and 15.3 to 39.2 µg/kg, respectively [65], whereas, the Korean Special Management Sea Areas also reported high values of diuron concentration (i.e., <0.06 to 144 µg/kg) [48]. The study conducted in Indonesian coastal areas reported diuron concentration between 0.04 and 740 μg/kg and this concentration was the highest compared to other studies conducted in Asian coastal areas.

Table 3. Concentration of booster biocide compounds in sediment collected from seagrass area of Sungai Pulai estuary (μg/kg).

Point	n	Diuron	Dichlorofluanid	Chlorothalonil	Irgarol 1051	M1	Sea-nine 211
		Mean ± SD					
Point 1	3	<0.1	48.7 ± 2.4	<0.1	0.14 ± 0.01	44 ± 2.2	9.1 ± 0.5
Point 2	3	3.4 ± 0.2	108 ± 5.4	<0.1	<0.1	82.5 ± 4.1	20.2 ± 1.0
Point 3	3	22.9 ± 1.1	800 ± 40	6.2 ± 0.3	1.4 ± 0.1	876 ± 44	170 ± 8.5

SD: Standard deviation.

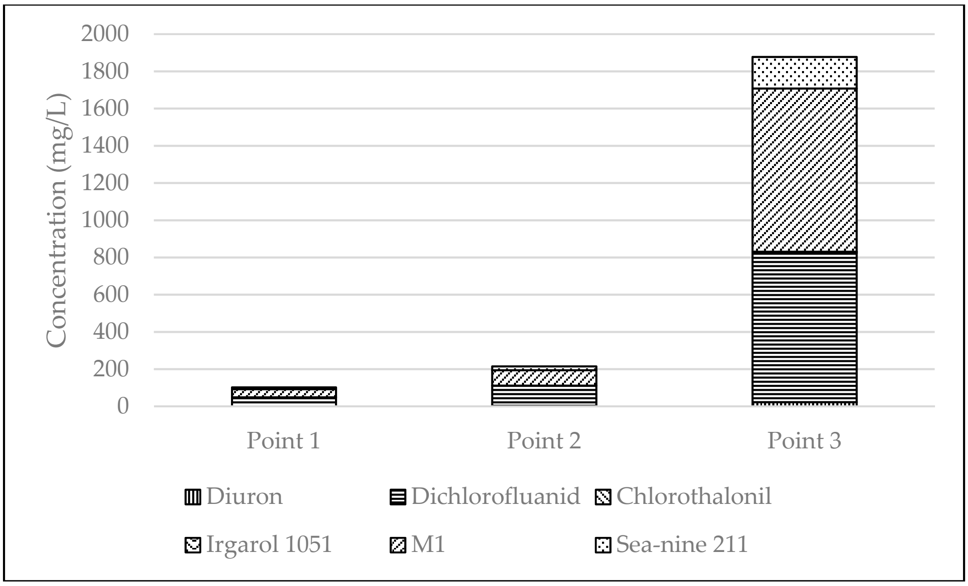

Figure 2. Concentration of booster biocides compound on seagrass bed of Sungai Pulai.

Compared to other countries, Irgarol 1051 in the sediments had low concentration with the range of <0.1 to 1.4 ± 0.1 μg/kg. In South East Asia, studies on Irgarol 1051 in sediments have been performed in a number of countries including Thailand [52], Vietnam [66], Malaysia, [37] and Indonesia [31] with the ranges of <0.03 to 3.27, 0.05 to 4, <0.02 to 14, and 0.1 to 80 μg/kg, respectively. The highest concentration of Irgarol 1051 in the coastal area of Malaysia was detected in the Malacca Port where aquaculture activities are conducted and it is a port for the mooring of small fishing boats. Meanwhile, the highest concentration of Irgarol 1051 in Indonesia was in Bitung, the main area of fishery industries; besides, large ships from Malaysia and Singapore are moored at and sailing in and out of Bitung port. The studies have proven that Irgarol 1051 is used as an ingredient in antifouling paint in South East Asian countries. The concentration of Irgarol 1051 in this study was the lowest compared to other South East Asian countries. The concentration of Irgarol 1051 in sediments has also been recorded internationally. The ranges of concentration of Irgarol 1051 for southern England [67], French Mediterranean coast [68], Californian marinas [69], as well as Busan and Ulsan Bay in Korea [65] were from <1.7 to 45, 43 to 689, <0.3 to 8.9, 1.79 to 73.5, and <0.02 to 38.8 μg/kg, respectively. The high concentration of Irgarol 1051 in the French Mediterranean coast was due to ship chandlers and this value is comparable to the values in other location, for example, Orwell Estuary, United Kingdom [70] which had the values of <10 to 1011 μg/kg. Although Irgarol 1051 has a relatively low affinity for particulate matters (log KOC 3.0; log KOW 3.9); however due to low water exchange in ports and marinas, this might result in the presence of this biocide in the areas and the biocide is able to partially bind with sediments [71,72].

The concentration of Sea-Nine 211 in the sediments was in the range of 9.1 ± 0.5 to 170 ± 8.0 µg/kg. These values are comparable with other study sites such as the coast of Indonesia [31], Korea [65], and also Otsuchi [53] and Hiroshima bay in Japan [73] with the concentration of <0.04 to 150, <0.02 to 281, <0.04 to 150 and 7.6 to 140 µg/kg, respectively. These areas are busy with shipping activities and there is a possibility for the release of higher booster biocide concentration into the marine ecosystems. The half-life of Sea-Nine 211 examined in laboratory studies and under controlled field conditions is less than 24 h [74,75]. Environmental conditions including sunlight reduce the Sea-Nine 211 concentration and the low detection of Sea-Nine 211 in sediments is due to rapid degradation of the biocide in the water column [76].

In this study, the concentration of chlorothalonil was in the range of <0.1 to 6.2 ± 0.30 µg/kg. In selected Greece ports and marinas, the values of chlorothalonil detected in sediments were from 8 to 165 µg/kg [77]. Chlorothalonil was also detected in the sediment samples from Blackwater Estuary, United Kingdom. The concentration was detected with values ranging from 16 to 34.3 µg/kg [78]. The compound is highly and widely spread, and consistent with its use in agriculture, although its half-life is only about 1.8 days. In another study in the coastal water of United Kingdom, no chlorothalonil was detected in sediments [74]. Since chlorothalonil has short half-life, the concentration is mostly low in many regions. This compound involves photodegradation as the basic mechanism and if it does not degrade in the water column, it will settle into sediments, where there is no light present and it will possibly give continuous and prolonged influence [79].

Dichlofluanid was detected in the sediments with the concentration of 48.7 ± 2.4 to 800 ± 40 µg/kg. Various studies have detected dichlofluanid with low concentrations. The concentrations recorded for the studies were <0.1, <0.4 to 14, <0.1 to 13, 12 to 65, and <0.04 to 80 µg/kg for the sediment samples collected from Peninsular Malaysia [37]; Otsuchi Bay, Japan [53]; Vietnamese coastal areas [66]; Catalonia, Spain [80]; and Indonesian marinas [31], respectively. However, the value obtained from the current study was comparable with the study of Blackwater Estuary, United Kingdom, which had the highest dichlofluanid concentration of 688 µg/kg [78]. Many studies have shown low concentrations of dichlofluanid and this coincides with the shortest half-life in chemical hydrolysis degradation [81]. The degradation of dichlofluanid in the natural environment has a half-life of 18 h, which is a rapid degradation process [82].

4. Conclusions

The contamination by OTs and booster biocides were widely distributed and detected in the surface sediment of the seagrass bed in Sungai Pulai estuary. From the investigation, among OTs compound, PTs were detected to be higher than BTs in the sediments. Meanwhile, the concentration of booster biocides was greater than OT compounds. This indicates booster biocides have substituted OT compounds at these sites and contamination by booster biocides is a more serious issue than OTs in coastal water nowadays. The variations of concentration were associated with the current activities conducted in this particular area, the ocean tidal that affects the movement of sediment, and geological condition of marine ecosystem. Further study is needed to monitor OT and booster biocides in developing countries and evaluate the risk of booster biocides as it is estimated that the demand for these compounds will increase in the future.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used “Conceptualization, A.M., F.M.-Y. and S.Z.Z.; Methodology, A.M. and H.H.; Validation, A.M., F.M.-Y. and H.H.; Formal Analysis, A.M.; Investigation, A.M. and S.Z.Z.; Resources, A.M. and H.H.; Data Curation, A.M.; Writing-Original Draft Preparation, A.M.; Writing-Review & Editing, F.M.-Y. and S.Z.Z.; Visualization, F.M.-Y.; Supervision, S.Z.Z.; Project Administration, S.Z.Z., and A.I.; Funding Acquisition, A.I.”.

Funding: This research was funded by the Fundamental Research Grant Scheme (FRGS) (Reference No.: FRGS/1/2014/STWN01/UPM/02/4) from the Ministry of Higher Education, Malaysia and was performed in relation to the JSPS Core-to-Core Program, B. Asia-Africa Science Platforms.

Acknowledgments: We are grateful to the members of the Faculty of Science, Universiti Putra Malaysia, in particular to Abdullah Talib and Azizul Aziz for their involvement in sampling and laboratory activities.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

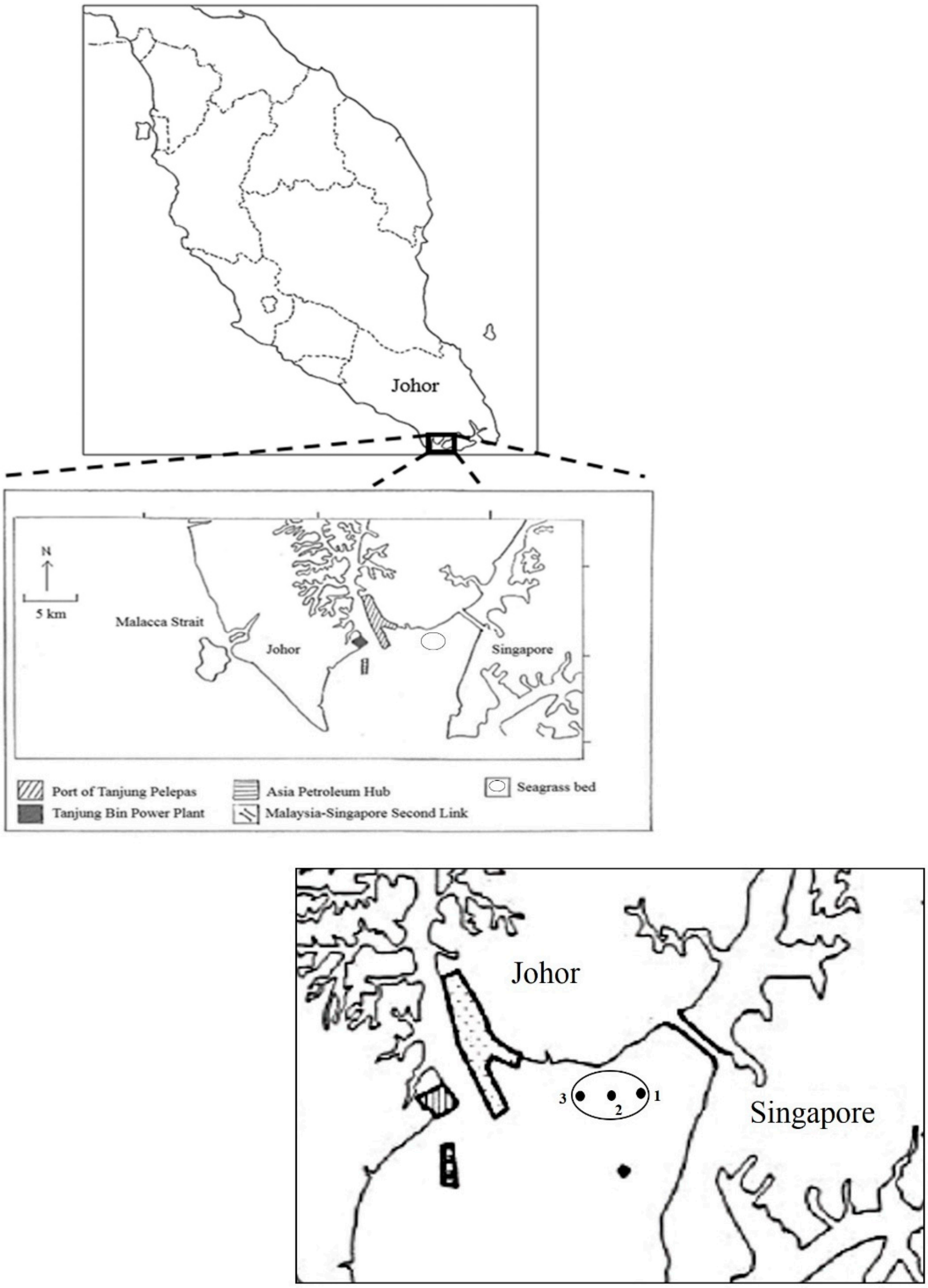

Figure A1. Seagrass area of Sungai Pulai Estuary in south of Johor.

Table A1. Concentration of organotin compounds in sediment (μg/kg).

Location	MBT	DBT	TBT	MPT	DPT	TPT	Reference
Semi-closed Port of Gdynia	134–1125	250–3810	1143–6743	n.r.	n.r.	n.r.	[44]
Indonesian coastal waters	1.5–170	0.9–78	0.4–350	0.2–22	<0.1–39	<0.1–19	[31]
Fishing ports along the Chinese coast	<3.6–194	<2.3–41.5	<0.7–86	n.r.	n.r.	n.r.	[45]
Southern Baltic coastal zone	0.54–33.97	0.51–38.66	0.2–115.2	n.r.	n.r.	n.r.	[46]
Kaohsiung Harbor, Taiwan	0.5–83.4	0.5–31.6	1.2–112	n.r.	n.r.	n.r.	[47]
Shipping and shipbuilding areas in South Korea	15–6212	4–8747	3–55,264	n.r.	n.r.	n.r.	[64]
Korean Special Management Sea Areas	<0.1–56.9	<0.1–160	<0.1–2304	<0.1–46.7	<0.1–2.33	<0.1–68.5	[48]

Table A2. Concentration of booster biocide compounds in sediment (μg/kg).

Location	Diuron	Dichlofluanid	Chlorothalonil	Irgarol 1051	M1	Sea-Nine 211	Reference
California marinas	<0.3–4.2	n.r.	n.r.	<0.3–8.9	<0.3–5.3	n.r.	[69]
Shipping and shipbuilding areas in South Korea	2.3–62.3	n.d.	n.r.	n.d.–11.5	<0.2–0.6	<0.2–5.5	[64]
Korean Special Management Sea Areas	<0.06–144	n.r.	n.r.	<0.02–7.79	<0.07–0.9	<0.06–117	[48]
Malaysian coastal area	<0.02–4.8	<0.1	n.r.	<0.02–14	<0.1	<0.04–1.7	[37]
Thailand coastal area	<0.08–25	n.r.	n.r.	0.03–3.2	<1	0.09	[52]
Vietnamese coastal areas	0.11–3.0	<0.01–13	n.r.	0.05–4.0	<0.1–0.43	0.09–1.3	[66]
Indonesian coastal waters	<0.04–740	<0.04–80	n.r.	0.1–76	0.4–670	<0.04–150	[31]
Panamanian marinas	<0.75–14.1	n.r.	n.r.	<0.08–2.8	n.r.	<0.38–81.6	[63]
Busan Bay, Korea	6.89–29.9	n.r.	22–1065	1.79–73.5	n.r.	61.2–269	[65]
Ulsan Bay, Korean	15.3–39.2	n.r.	1.3–422	<0.02–38.8	n.r.	<0.02–264	[65]

n.r.: no record; n.d.: not detected.

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