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Monitoring of Butyltin Compounds in the Aquatic Environments of the Philippines

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Abstract — A comprehensive perspective of Butyltin (BTs) contamination and its possible implications on the marine and coastal environments of the Philippines is presented using green mussels, marine mammals and skipjack tuna as bioindicators. BTs were detected in mussels from all the sampling locations investigated as part of the monitoring surveys under the Asia-Pacific Mussel Watch (APMW) Program conducted in the late 1990s. The BTs detected in green mussels collected in 1994, 1997 and 1998 from various aquaculture and coastal sites in the country were suggestive of considerable widespread pollution by BTs in the coastal waters. Among BTs, TBT was detected at all locations at relatively higher concentrations, whereas the concentrations of DBT and MBT were found to be at lower residual concentrations. This could be indicative that green mussels have limited ability of metabolize TBT to DBT and MBT. It could also be suggestive of recent TBT inputs into the aquatic environments and the presence of sources along the coastal waters. Concentrations of BTs (MBT+DBT+TBT) in green mussels were reported up to 790 ng g^{-1} wet weight in a site where intensive maritime activities are occurring. Mussels from rural areas contained TBT at lower proportions indicating that TBT usage as antifouling agents is minimal. Tolerable Average Residue Level (TARL) for seafood in the Philippines was estimated at 173 ng g^{-1} wet weight for an average person weighing 60 kg. Concentrations of TBT or the sum of TBT and DBT in some green mussels analysed revealed that some values exceeded TARL level, which could suggest that humans consuming this seafood from areas with high BTs contamination could be at risk from elevated exposure to BTs. BTs were likewise detected in skipjack tuna collected from the offshore waters of the Philippines, suggestive of the widespread contamination even in offshore waters. Considerable BTs levels (up to 220 ng g^{-1} wet weight), with high percentages of BTs in total tin (∑Sn: inorganic tin+organic tin) were noted in the liver tissues. This finding indicates that the anthropogenic BTs represent the major source of Sn accumulation. On the other hand, relatively low concentrations of BTs were found in the liver of cetaceans from the coastal waters of the Philippines, which ranged at 42–98 ng g^{-1} wet weight. Significantly lower hepatic BT concentrations in cetaceans in tropical waters were noted compared with those inhabiting temperate waters proximal to developed nations. This result could imply that, at present, usage of BTs in the Philippines is still minimal.

Key words: butyltins, green mussels, skipjack tuna, marine mammals, Philippines, aquatic environments

Introduction

Over the last two decades, rapid increase of chemical trade in developing countries in Asia was recognized, which implied greater production and usage of toxic chemicals such as heavy metals, organochlorines and butyltins. These activities could lead to increase exposure of humans and wildlife to these chemicals (Tanabe 1999). Consequently, environmental problems associated with these persistent organic pollutants became a serious concern, particularly in the aquatic environment.

Since the 1960s, BTs have been widely used for maritime structures, aquaculture activities, lumber preservatives and slimicides in cooling system, and as an effective antifouling agent in paints (Sudaryanto et al. 2002). Its derivatives-dibutytin (DBT) and monobutyltin (MBT) were mostly used as stabilizers in polyvinyl chloride and as catalysts in the production of polyurethane foams, silicones, and in other industrial processes (Fent 1996). Widespread usage of butyltins motivated the conduct of numerous studies in order to elucidate environmental contamination and impacts. Considerable studies reported adverse effects of BTs on non-target marine organisms, such as shell malformation in oysters (Alzieu and Heral 1984, Alzieu and Portmann 1984), mortality on the larvae of mussels (Beaumont and Budd 1984), and imposex in gastropods (Bryan and Gibbs 1991). In view of these investigations, aquatic pollution by BTs has been given much attention in many countries, which eventually led to its restriction, particularly the TBT-based antifouling paints, in most developed nations since the 1980s. However, in most developing Asian countries, including the Philippines, such control is yet to be enforced. In addition, an increasing demand for antifouling paints is expected in the Asia-Pacific region (Layman 1995). Thus, ecotoxicological studies have underscored the need to give considerable attention to the aquatic pollution and toxic biological effects by BTs in this region.

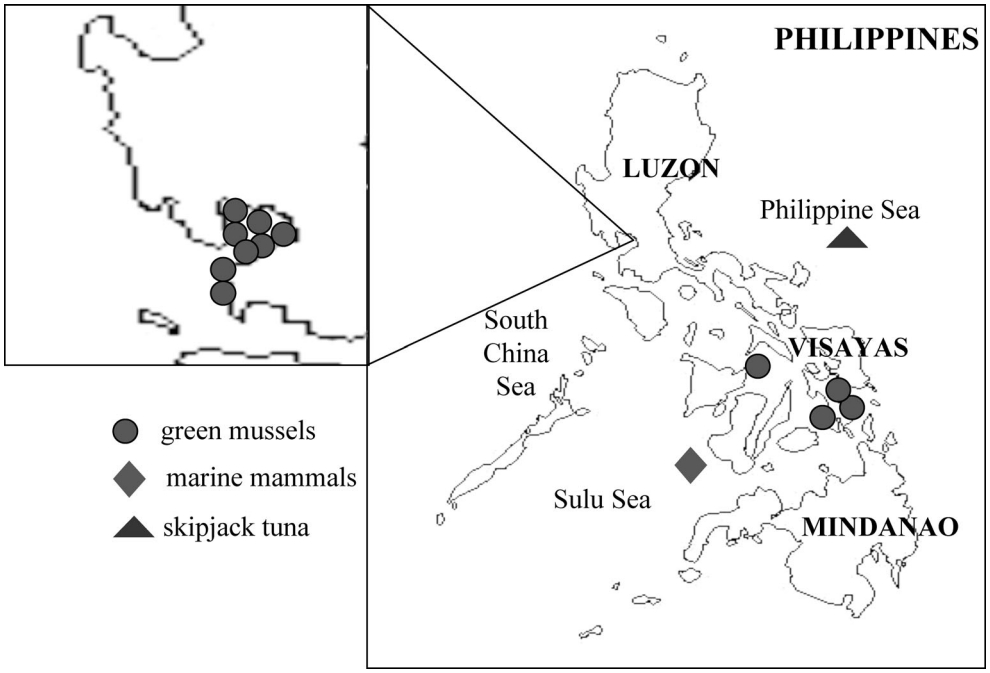

Fig. 1. Sites considered for the collection of green mussels, marine mammals and skipjack tuna from the coastal and offshore waters of the Philippines.

In the Asia-Pacific region, the green mussel *Perna viridis* is widely distributed along the coasts and is considered to be a commercially valuable seafood (Vakily 1989). Since 1994, monitoring studies in connection with the Asia-Pacific Mussel Watch Program (APMW), aimed at monitoring the pollution in Asian coastal waters have been conducted. Results presented here form part of the collaborative research project among scientists from Cambodia, Hongkong, India, Indonesia, Korea, Malaysia, the Philippines, Thailand, Vietnam and Japan through the Asia Pacific Mussel Watch Project. Furthermore, in an effort to extend the conduct of continuous and comprehensive monitoring survey of BTs in the ocean environment, widely distributed and globally migrating organisms such as marine mammals and skipjack tuna were also considered for further investigations by the same group of collaborating scientists from the Asia-Pacific region. As one of the participating scientists in these cooperative research investigations, this paper is presented to elucidate the contamination by BTs in the aquatic environments of the Philippines. Residual concentrations of BTs in green mussels, skipjack tuna and marine mammals collected along strategic aquatic locations in the Philippines are described and discussed. Moreover, in order to determine the degree of contamination in these waters, concentrations of BTs detected were compared with reported values from other regions.

Materials and Methods

Samples

Whole soft tissues of green mussels *Perna viridis* from various coastal sites; liver tissues of marine mammals including Fraser's dolphin *Lagenodelphis hosei* and spinner dolphin *Stenella longirostis* from the northeastern part of Sulu Sea; and liver tissues of skipjack tuna collected from the marine waters off the Philippines were considered for the analysis of BTs residues (Fig. 1).

More than 30 green mussels were collected from each location and the adhering matrix was removed in the field. Mussel samples were stored in polyethylene bags, kept in a cooler box with dry ice and then immediately kept in a deep-freezer. The frozen mussels were subsequently transported to the laboratory, biometric data measured (Table 1), thawed, scraped clean and shucked. The whole soft tissues were pooled, homogenized, then kept in clean glass bottles. All samples were frozen at −20°C until chemical analysis. On the other hand, after dissection of the marine mammals and skipjack tuna employed for this study, the liver tissues were likewise stored in polyethylene bags at −20°C until analyses.

Chemical Analysis

For the whole soft tissues of the green mussels: the analytical method of BTs was conducted based on the procedure previously described (Kan-atireklap et al. 1997). Briefly, the method consists of extraction, propylation, purification and quantification by Hewlett-Packard 5890 Series II gas chro-

Table 1. Biometric data of green mussels collected from coastal waters of the Philippines.

Location	Sampling date	n	Shell length (mm)	Soft tissue weight (g wet wt)
Paranaque, Metro Manila	941122	32	40 (35–50)	1 (0.8–2)
Ermita, Manila Bay	941125	19	47 (40–57)	3 (2–6)
Malate, Manila Bay	941127	32	54 (48–63)	3 (1–4)
Bocaue, Bulacan	941128	41	65 (51–80)	4 (2–8)
Bacoor, Cavite	941130	39	63 (54–80)	4 (2–6)
Bocaue, Bulacan	970411	29	66 (57–80)	8 (5–13)
Bacoor, Cavite	970409	30	77 (63–109)	12 (7–26)
Jiabong, Samar	970404	30	77 (48–100)	7 (2–11)
Villareal, Samar	970405	30	76 (63–86)	8 (6–11)
San Pedro Bay, Leyte	970406	30	78 (62–114)	5 (2–14)
Sapian Bay, Capiz	970407	18	76 (69–87)	5 (4–7)
Samal, Bataan	970408	51	46 (35–53)	3 (2–5)
Malabon, Metro Manila	970410	30	68 (58–80)	10 (5–16)
Pamarawan, Bulacan	980326	15	81 (74–93)	8 (6–10)
Obando, Bulacan	980317	82	58 (17–89)	4 (2–10)
Malabon, Metro Manila	980316	71	63 (41–87)	6 (2–14)
Bacoor, Cavite	980327	43	69 (60–77)	7 (5–19)
San Pedro Bay, Leyte	980321	15	104 (89–117)	17 (13–27)
Jiabong, Samar	980322	46	67 (50–95)	5 (2–13)
Villareal, Samar	980323	51	67 (51–84)	4 (2–8)
Sapian Bay, Capiz	980408	87	64 (41–87)	4 (2–10)

matograph equipped with a flame photometric detector (GC-FPD). For quantification of BTs, a fused silica capillary column (J & W Scientific Co. Ltd., 30 m length×0.25 mm i.d., 0.25 μm film thickness) coated with DB-1 (100% dimethyl polysiloxane) was used. Recoveries of BTs from the spiked mussel tissues were 87±14%, 137±20% and 107±25% for MBT, DBT and TBT (n=7), respectively. The detection limit was 3 ng g^{-1} for MBT and 1 ng g^{-1} for DBT and TBT.

For the liver tissues of the marine mammals and skipjack tuna: the chemical analysis of BTs was conducted following the method previously described (Iwata et al. 1995). Briefly, about 1–2 g of liver tissue was homogenized with 1 N HCl and 0.1% tropolone/acetone. The BTs in extracts were transferred to 0.1% tropolone/benzene, and the moisture in the solvent was removed with anhydrous Na_2SO_4, followed by transferring the solvents to hexane. BTs in hexane were propylated by adding propyl magnesium bromide as a Grignard reagent. The extract was added on a dry florisil column and passed with nitrogen gas slowly. BTs adsorbed on the florisil were eluted with 20% water/acetonitrile to remove lipid. The eluate was then subjected to a wet florisil column for further purification. The final extract was injected into a gas chromatograph with flame photometric detector and a tin mode filter (610 nm). A fused silica capillary column (DB-1; 0.25 mm i.d.×30 m length) was used for separation. Identification of BTs was made by assigning peaks in samples to corresponding peaks of external standard. Peak heights of individual BTs were used for quantification. Standard mixtures were prepared with every set of four samples by propylating the known amounts of BT ion mixtures spiked on an Antartic minke whale liver, which was previously found to contain trace levels of BTs. Hexyl-tributyltin was added as an internal standard. Accuracy of the analytical method was checked using a certified biological reference material and results showed a good agreement with the certified value. Concentrations in samples were not corrected for recoveries. Concentrations of BTs are reported as nanograms of cation per gram on a wet weight basis, unless otherwise specified. In addition, concentrations were also calculated on a dry-weight basis based on the moisture contents of the samples.

In the case of the skipjack tuna, the analytical procedure for total tin ($\sum$Sn) was based on the method described elsewhere (Le et al. 1999) with a slight modification. Briefly, tissue samples were dried at 80°C for 12 h and then homogenized into powder. About 1 g of sample was weighed into 8 ml PTFE tubes. Digestion was carried out with purified HNO_3 (~63%) in a microwave oven at 200 W. After digestion, the sample was transferred into a measuring flask and diluted with Milli-Q water (Millipore, Bedford, MA, USA). Tin concentrations in samples were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Hewlett-Packard, HP4500). Detection limit was 10 ng Sn g^{-1} on a dry weight basis. The recovery of Sn in this method was checked by analysing a certified material (NIES No. 11), and our result (2.5±0.1 μg Sn g^{-1}, n=4) agreed well with the certified value ((2.4±0.1 μg Sn g^{-1}).

Table 2. Concentrations (ng g^{-1} wet weight) of butyltin compounds (BTs) in green mussels collected from Philippine coastal waters.

Location	Area description	MBT	DBT	TBT	BTs*
1994					
Paranaque, Metro Manila	Urban area, aquaculture area	15	13	76	104
Ermita, Manila Bay	Harbor, shipping line, urban area	47	100	640	787
Malate, Manila Bay	Harbor, shipping line, urban area	51	43	200	294
Bocaue, Bulacan	Agriculture, aquaculture area	5	4	13	22
Bacoor, Cavite	Urban area, aquaculture area	9	8	34	51
Bocaue, Bulacan	Agriculture, aquaculture area	<3	12	34	46
1997					
Bacoor, Cavite	Urban area, aquaculture area	<3	16	43	59
Jiabong, Samar	Agriculture, aquaculture area	<3	3	1	4
Villareal, Samar	Agriculture, aquaculture area	<3	2	28	30
San Pedro Bay, Leyte	Agriculture, aquaculture area	<3	<1	<1	<1
Sapian Bay, Capiz	Agriculture, aquaculture area	<3	1	<1	1
Samal, Bataan	Agriculture, aquaculture area	<3	<1	<1	<1
Malabon, Metro Manila	Urban area, aquaculture area	3	15	44	62
1998					
Pamarawan, Bulacan	Agriculture, aquaculture area	<2.0	2.1	1.7	3.8
Obando, Bulacan	Agriculture, aquaculture area	7.7	5.8	3.9	17
Malabon, Metro Manila	Urban area, aquaculture area	8.1	19	47	74
Bacoor, Cavite	Urban area, aquaculture area	15	18	31	64
San Pedro Bay, Leyte	Agriculture, aquaculture area	4.7	2.8	9.8	17
Jiabong, Samar	Agriculture, aquaculture area	<2.0	<1.3	0.8	0.8
Villareal, Samar	Agriculture, aquaculture area	<2.0	<1.3	0.8	0.8
Sapian Bay, Capiz	Agriculture, Aquaculture area	2.1	1.6	3	6.7

*BTs=MBT+DBT+TBT

Results and Discussion

Contamination status, distribution and pollution sources of BTs in the aquatic areas of the Philippines is hereinafter discussed by considering the residues found in the whole soft tissues of green mussels and in the liver tissues of skipjack tuna and marine mammals analysed.

Green mussels. Among the BTs, TBT was detected in most of the sampling sites at relatively high concentrations, whereas the concentrations of DBT and MBT were lower (Table 2). Concentrations of BTs in green mussels collected in 1994–98 ranged from <2 to 51 ng g^{-1} for MBT, <1 to 100 ng g^{-1} for DBT and <1 to 640 ng g^{-1} for TBT. Relatively high TBT concentrations were observed in samples collected from Manila Bay, where maritime activities are quite intensive, considering that is a major shipping traffic area with large harbours. Concentrations of BTs (MBT+DBT+TBT) in mussels from Manila Bay were found to range at 104 ng g^{-1} to 787 ng g^{-1}, suggestive that the source of TBT could be antifouling paints. Previous studies have likewise documented the existence of TBT contamination in harbours, marinas, shipyard hull washing/refinishing and boating activities (Maguire et al. 1982, Page et al. 1996, Horiguchi et al. 1994). On the other hand, BTs levels were found to be low in green mussels collected from aquaculture areas (ranging from <1 ng g^{-1} to 4 ng g^{-1}), implying minimal usage of BTs for aquaculture activities in the Philippines. Thus, it is probable that the major BTs pollution sources in the country are far sea or commercial vessels that could be using TBT-coated antifouling agents on the ship hulls. These findings also indicate that BTs contamination seem to be widespread along Philippines' coastal waters (Prudente et al. 1999). TBT levels (ranging <1 to 640 ng g^{-1}) found in mussel samples from Philippine waters were comparable with those in Thailand, but were higher than those in other Asian countries such as Malaysia and Hongkong (Fig. 2). Similar to Thailand (Kan-atireklap et al. 1997), pollution of BTs in the Philippines may be considered to be "high" among Asian developing countries so far reported. However, when compared with recent surveys of other bivalve species from various locations, the BTs levels in Philippines were still lower than those in developed nations.

The compositional ratio of butyltin derivatives in *P. viridis* analysed was observed to be in the order of TBT>DBT>MBT. Among BTs, TBT was the dominant compound occupying about 70% in most locations, while DBT and MBT comprised less than 30%. These findings conform with the observations made by Kan-atireklap et al. (1997) on the limited ability of *P. viridis* to metabolize TBT to DBT and MBT similar to other molluscs. Such limitation was explained by the low cytochrome P-450 content and mixed

function oxygenase activity in molluscs (Lee 1991, 1995). Additionally, continuous input of TBT in the coastal waters of the Philippines may also provide a plausible explanation for the higher ratio of TBT found in mussel samples analysed. It is interesting to note however, that mussels from rural areas contained TBT at lower concentrations and proportions, indicating that TBT usage as antifouling agents in these rural areas seems to be minimal. A possible pollution source of BTs in these locations may be the usage of MBT and DBT in plastic products as stabilizers and catalysts. In fact, plastic has often been found along the coasts of Asian developing countries, even in rural sites (Sudaryanto et al. 2002).

Since mussels are one of the commonly consumed seafood items in the country, it is worthwhile to assess possible risk to human health. In an earlier study conducted by Sudaryanto et al. (2002), it was pointed out that to assess risk to human health from the consumption of seafood products, tolerable average residue levels (TARLs) as suggested by Belfroid et al. (2000) could be calculated as

$$\mathrm{TARL} = \frac{(\mathrm{TDI} \times 60\ \mathrm{kg\ body\ weight})}{\mathrm{Average\ daily\ seafood\ consumption}}$$

Using the data of average seafood consumption reported by Food and Agriculture Organization (FAO) of the United Nations, TARL for seafood in the Philippines was estimated at 173 ng g^{-1} wet weight for an average person weighing 60 kg (Sudaryanto et al. 2002). Concentrations of TBT or the sum of TBT and DBT (TBT+DBT) in some of the mussels analysed were found to have exceeded this value, which could be suggestive that people consuming seafood from areas with high butyltin contamination may be at risk from elevated exposure to BTs.

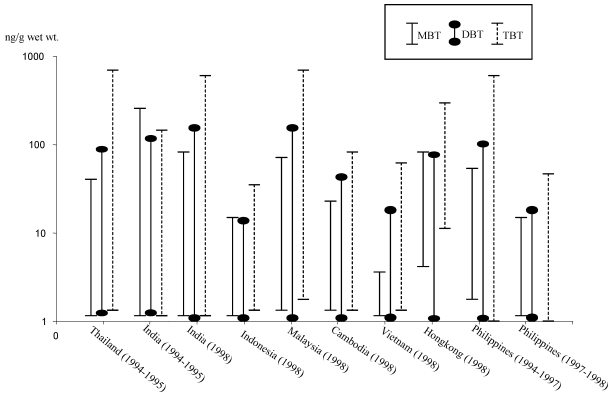

Fig. 2. Range concentrations of MBT, DBT and TBT residues in green mussels from APMW project from 1994–1998 (Kanatireklap et al.,1997, Prudente et al., 1999 and Sudaryanto et al., 2002).

Sudaryanto et al. (2002) evaluated the extent of anthropogenic input of tin by determining the residues of total tin (∑Sn: organic Sn+inorganic Sn) against the BTs residues found in green mussels collected in 1998 in some coastal and aquaculture areas in the Philippines. It was reported that the ratio of BTs in ∑Sn were higher in the coastal areas where high boating activities are occuring. These observations indicate that anthropogenic sources contribute considerably in tin accumulation in green mussels and that most of the total tin in mussels exists in organic form such as BTs, which further imply that tin compounds originated mostly from anthropogenic sources.

Marine mammals. Relatively low concentrations of BTs were measured in the liver of cetaceans from the Sulu Sea, which ranged at 42–98 ng g^{-1}, wet wt. (Table 3). These findings were similar to the low BTs residues (ranging <1–30 ng g^{-1} wet wt.) found in green mussels from the waters in the Visayas region, which is proximal to the site where these marine mammals were collected. BTs residue levels in these cetaceans compare favorably with those found in cetaceans collected from China (350 to 1200 ng g^{-1}, wet wt), another developing country in Asia (Tanabe et al. 1998). Further, it can be seen in Figure 3 that cetaceans inhabiting waters adjacent to developing countries in the tropics and subtropics including the Philippines and India contain significantly lower hepatic BT concentrations compared with those inhabiting temperate waters proximal to developed nations such as Japan (Tanabe et al. 1998). This could be indicative of significant and continuous inputs of BTs in the coastal waters of these developed countries, while smaller usage in developing countries, such as the Philippines, is implied at least at present.

Table 3. Concentrations (ng g-1wet weight) of butyltins in the liver of cetaceans from Sulu Sea and Philippines.

Species	WBL* (cm)	N M	N F	MBT	DBT	TBT	BTs
Lagenodelphis hosei	221–225	1	1	15	53	26	94
Fraser's dolphin				(<4.0–29)	(38–68)	(21–31)	(89–98)
Stenella longirostris	182–192	1	1	2	32	21	55
Spinner dolphin				(<4.0–3.1)	(23–41)	(19–23)	(42–67)

* WBL: Whole body length (cm); N: no. of samples.
BTs=MBT+DBT+TBT
Bold: mean concentration. Ranges are given in parentheses.

Among the BTs, DBT was predominant in most of the liver samples of these marine mammals, followed by TBT and MBT. This pattern is similar to BTs composition observed in other cetaceans previously studied, which includes harbour porpoises from the Black Sea (Madhusree et al. 1997), bottle-nosed dolphins along the coasts of Italy (Kannan et al. 1996), and stranded cetaceans along the U.S. Atlantic and Gulf coasts (Kannan et al. 1997). These findings are indicative of similar metabolic processes among cetaceans. It has been reported that butyltins appear to be higher in the liver of cetaceans than pinnipeds, due at least in part to the ability of some pinnipeds to shed BTs in the hair during moulting (Kim et al. 1996). Moreover, BTs were reported to be higher in marine mammals of coastal Pacific waters rather than the open ocean (Tanabe et al. 1998, Tanabe 1999). Interestingly, higher accumulations of DBT/BTs than TBT/BTs were detected in spinner and dolphins collected from the the Sulu Sea, Philippines. In contrast, the same species of spinner dolphins collected from Bay of Bengal, India revealed higher ratio of TBT/BTs than DBT/BTs (Tanabe et al. 1998). The reason for the apparent difference in BTs composition among the spinner dolphins collected from India and the Philippines remains unclear. However, higher maritime activities in the Bay of Bengal than in Sulu Sea could be a plausible explanation.

While DBT in the liver of these marine mammals accounted for about 55% of total BTs detected, which fall within the same range as the reported levels in other developing countries in the tropics and sub-tropics (Tanabe et al. 1998). On the other hand, for cetaceans from developed countries, DBT contributed 55–75% of the total hepatic BTs (Tanabe et al. 1998). It has been reported that significantly lower MBT/∑BT and DBT/∑BT ratio observed in the marine mammals from developing countries could be indicative of lesser inputs of MBT and DBT, originating from stabilizers for chlorinated polymers etc., compared with inputs that were occurring in the coastal waters of developed nations (Tanabe et al. 1998).

Skipjack tuna. Mean and range concentrations of BTs and ∑Sn in the liver of skipjack tunas collected from offshore waters of the Philippines and the green mussels from various coastal waters is shown in Table 4. Concentrations of BTs in the liver tissues of skipjack tuna collected off Philippine waters in December 1997 ranged at 78–270 ng g^{-1} wet weight. Among BTs, TBT was detected at relatively higher concentrations, whereas DBT and MBT were lower. This pattern conforms with those observed in green mussels (Fig. 4), which seemingly indicate continuous inputs of TBT into the aquatic environment and the presence of recent sources in the offshore waters. In addition, skipjack tuna, similar to other molluscs and fishes may have a limited ability to metabolise

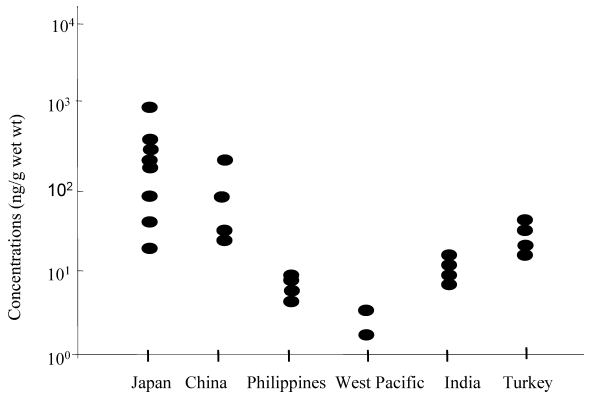

Fig. 3. Comparison of hepatic BTs concentrations in marine mammals from the Asia-Pacific region. Values for Turkey and other countries were from Madushree et al., 1997 and Tanabe et al., 1998, respectively.

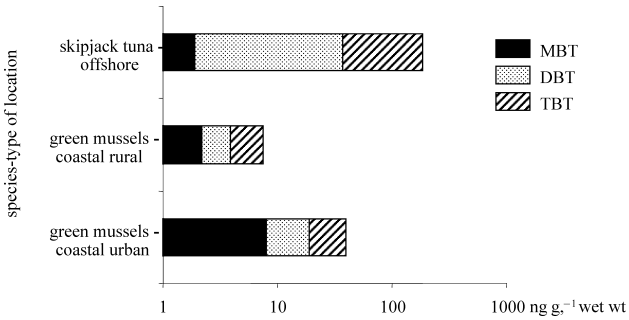

Fig. 4. Composition of butyltin compounds in the green mussels and skipjack tuna from the coastal and offshore waters of the Philippines, respectively.

Table 4. Mean and range of butyltins and total tin concentrations in green mussels and skipjack tunas collected from Philippine waters.

Species	Location	MBT*	DBT*	TBT*	BTs*	TBT/BTs (%)	∑BTs**	∑Sn**	∑BTs/∑Sn (%)
green mussels	urban coastal waters	7.9 (<2.0–15)	11 (2.1–19)	21 (1.7–47)	40 (3.8–74)	45 (23–64)	89 (9.6–150)	130 (28–180)	63 (28–107)
green mussels	rural coastal waters	2.2 (<2.0–4.7)	1.7 (<1.3–2.8)	3.6 ().8–3)	6.3 (0.8–17)	76 (45–100)	17 (1.6–74)	47 (17–74)	26 (4.2–64)
skipjack tuna	offshore waters	1.9 (< 1.8–5.7)	35 (16–66)	150 (62–200)	180 (78–270)	80 (75–86)	220 (95–310)	230 (140–320)	88 (68–100)

Bold: mean concentration; ranges are given in parentheses.
*ng g^{-1} wet wt
**ng Sn g^{-1} dry wt

TBT to DBT and MBT (Lee 1996, Ueno et al. 2004).

In order to understand the portion of anthropogenic input of tin (Sn), concentrations of total tin (∑Sn: sum of inorganic Sn+organic Sn) were determined and considerably high percentage of BTs in total tin (∑Sn: inorganic tin+organic tin) were found in the liver tissues of the tunas collected off-Philippines. Similar to the pattern observed in green mussels, this finding suggests that the anthropogenic BTs represent the major source of Sn accumulation in skipjack tuna. As reported by Ueno et al. (2004), BTs occupied higher percentages in ∑Sn concentrations in skipjack tuna collected from offshore waters around Asian developing countries having high concentrations of BTs, which suggested that hepatic Sn exists primarily in organic form as BTs that originate from anthropogenic sources. Considering the residues found in green mussels (Prudente et al. 1999, Sudaryanto et al. 2002), marine mammals (Tanabe et al. 1998) and skipjack tuna (Ueno et al. 2004), it is evident that BTs are widespread along coastal to offshore waters.

Conclusion

Significant butyltin concentrations in green mussels collected from the coastal areas of the Philippines revealed contamination along nearshore marine waters. Relatively high BTs concentrations were observed in green mussels collected from areas with intensive maritime activities, suggestive that antifouling paints could be the major TBT source. While low TBT levels found in green mussels from aquaculture areas imply minimal usage of BTs for aquaculture activities. Similarly BTs residues found in skipjack tuna collected from offshore waters of the Philippines indicated BTs contamination and presence of recent butyltin pollution sources. High percentages of BTs in ∑Sn found in the liver of the skipjack tuna suggest anthropogenic BTs as major source of tin accumulation in these animals. While the considerable BTs levels found in the liver tissues of marine mammals collected from Sulu Sea, and Philippines suggest that BTs accumulate at measurable levels in the liver of higher trophic marine animals. It seems evident from the BTs residues found in green mussels, marine mammals and skipjack tuna that BTs contamination is widespread along coastal to offshore waters. Considering the unregulated usage of TBT and the possible increasing demand for TBT-containing paints in the Philippines, contamination by BTs in its aquatic environments may become serious in the future. It is therefore necessary to conduct continuous monitoring in order to prevent the occurrence of possible adverse effects of BTs on the functional physiology of aquatic organisms and to make appropriate decisions on the future issues of butyltin contamination in the aquatic environments.

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