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Distribution and Specific Bioaccumulation of Butyltin Compounds in a Marine Ecosystem

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Abstract. Butyltin compounds (BTs), including tributyltin (TBT) and its breakdown products, di- (DBT) and monobutyltin (MBT), were determined in sea water, sediment, and biota at various trophic levels in the food chain collected from Otsuchi Bay, Japan, for understanding distribution and bioaccumulation of BTs in natural marine ecosystems. BT residues were detected in all the compartments analyzed, although their concentrations appeared to be less than those in polluted areas. Concentrations of BTs in sea water were higher in locations near Otsuchi Port, indicating that maritime activities in the harbor has been a major source of BTs in this bay. A specific peak in BT residue levels was found in sediment cores at an estimated depth that dated to be from the 1980s. Lack of significant variation in the composition of BTs at different depths of cores suggests slow degradation rate of these compounds in sediments. BTs were accumulated in plankton and other organisms up to ~70,000 times higher than in sea water. However, no considerable biomagnification was observed for BTs through the food chain. Relatively high concentrations were found in caprellids and smaller fish, such as gunnels. These organisms accumulated TBT as the predominant compound among BT derivatives and showed higher bioconcentration factors for TBT than in other species reported so far. Our results suggest that certain organisms in the food chain may have a less capacity to degrade TBT, and therefore may accumulate BTs at elevated levels.

Butyltins (BTs), one of the representative groups of organotin compounds, have been extensively used as polyvinyl chloride (PVC) stabilizers, industrial catalysts, biocides, wood preservatives, and antifouling agents in paints applied for boats and aquaculture nets since the 1960s. Aquatic pollution resulting from their usage has been of great concern due to their bioaccumulative potential and deleterious effects in organisms. Earlier studies have demonstrated that tributyltin (TBT) exerts chronic toxic effects on susceptible mollusks at water concentrations of a few ng L^{-1} (Alzieu 1996; Gibbs and Bryan 1996). The toxic concentrations of TBT at embryonic and early life stages of organisms lie in the range of a few µg L^{-1} or even lower (Bryan and Gibbs 1991; Maguire 1996; Fent 1996; Laughlin *et al.* 1996). In addition, sublethal effects such as immunotoxicity of TBT in fish and mammals possibly occur at environmentally exposed levels (Boyer 1989; Schwaiger *et al.* 1992; Rice *et al.* 1995). More recent studies have reported that TBT alters the activity of cytochrome P450 monooxygenases in organisms (Fent 1996; DeLong and Rice 1997; Kim *et al.* 1998) and disrupt the endocrine system in some species (Matthiessen and Gibbs 1998).

Concern over the ecotoxicological impacts of TBT led to restriction in most developed countries in the late 1980s. The restriction on TBT usage as an antifouling agent for coastwise boats and aquaculture nets has also been implemented in Japan in 1990. However, it is still being used for oceanliners and far-sea fishery boats and ships. Although a reduction in TBT contamination was recorded after the ban (Environment Agency Japan 1995), TBT concentrations in Japanese coastal waters still persist at levels considered to be toxic to susceptible organisms. Widespread occurrence of imposex in Japanese gastropods has been shown recently as a consequence of organotin pollution (Horiguchi *et al.* 1995). Furthermore, higher aquatic organisms, such as marine mammals and fish-eating birds, from the coastal areas of Japan accumulated BTs at µg/g levels (Iwata *et al.* 1995; Kim *et al.* 1996a; Guruge *et al.* 1996; Tanabe *et al.* 1998). Significant BT residues were detected even in organisms collected from the aphotic bathyal zone around Japan (Takahashi *et al.* 1997). These findings imply the expansion of contamination and continuous threat of organotins in various aquatic ecosystems.

Although numerous investigations have been conducted on organotin contamination and their toxic effects in aquatic organisms, comprehensive studies on their accumulative profiles in an entire marine ecosystem are still scarce. Particularly, little is known about BT accumulation along the food chain including higher trophic organisms such as marine mammals. For persistent organochlorines, such as PCBs and DDTs, significant biomagnification to the higher trophic mammals through the aquatic food chain have been well documented (Tanabe *et al.* 1984; Tanabe and Tatsukawa 1991). On the other hand, more recent studies showed that some of the characteristics of BT accumulation in fish and marine mammals were different from those observed for organochlorines. For instance,

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BTs have lower affinity to lipids than those of organochlorines (Yamada and Takayanagi 1992; Kannan *et al.* 1995; Kim *et al.* 1996a; Takahashi *et al.* 1997) and less biomagnification capacity in prey-predator relationships (Bryan and Gibbs 1991; Iwata *et al.* 1995; Kim *et al.* 1996a, 1996b; Guruge *et al.* 1996; Kannan *et al.* 1997; Takahashi *et al.* 1997). The foodweb transfer of BTs, therefore, may be different from the pattern of persistent organochlorines. However, details of such aspects in the natural marine ecosystem are still unclear.

In the present study, BTs, including TBT and its breakdown products, di- (DBT) and monobutyltin (MBT), were determined in sea water, sediment, and biota at various trophic levels in the food chain including plankton, amphipods, mussels, ascidians, sea urchins, and several fish species collected from Otsuchi Bay, Japan. The results of this study were discussed in order to elucidate specific bioaccumulation profiles of BTs in the marine ecosystem as well as to describe their occurrence and distribution. The data of BT concentrations in the liver of Dall's porpoises collected near Otsuchi Bay (off Sanriku), cited from our earlier study on cetaceans (Tanabe *et al.* 1998), were also associated in this study to assess the biomagnification in the higher trophic mammals.

Materials and Methods

Samples

Sea water, sediment, and biological samples were collected from Otsuchi Bay, Japan (Figure 1), from September 1994 to August 1995 under a biological research program by Otsuchi Marine Research Center (OMRC), Ocean Research Institute, University of Tokyo. Otsuchi Bay is located in the Pacific coast of northern Japan, is referred to as ''Sanriku Coast,'' and has a deeply indented coastline that is known typically as Rias Coastline. The entrance of this bay is deep (~80 m depth) and opens into the Pacific Ocean, resulting in well water exchange between inside and outside the bay (Shikama 1980). Compared with areas close to a metropolis, human activities are not so high along the coastal area of Otsuchi Bay, except for the harbor of Otsuchi Port with a small shipyard and fishery boats.

Sea water (n = 7), sediment core (n = 2), and net-plankton samples (n = 6) were collected from several sampling stations within and outward the bay (Sts. 1 to 7 in Figure 1), during August 1 and 2, 1995, using a small research boat of OMRC. Seawater samples were collected at 0.5 m below the surface with 1-L polycarbonate bottles rinsed with dilute hydrochloric acid (HCl). The sea water collected was immediately acidified with 1 ml of 12 N HCl, and extracted without filtration (see Chemical Analysis section). Solvent (0.1% tropolone-benzene) extracts from the sea water were stored at 4°C in the dark until chemical analysis. Sediment cores of 5.0-cm diameter and up to 10 cm depth were collected with a gravity corer. These sediments collected were slightly anoxic. Immediately after collection, the sediment from the cores was extruded in 1-cm slices, placed in butyltin-free polyethylene bags, and frozen in a deep-freezer at −20°C until analysis. Three sediment cores were collected at each station, and one set of sediment cores was employed for lead isotope ^{210}Pb analysis conducted at the Research Center of Radioisotopes, Osaka Prefecture University, to obtain geochronological data of the sediments. Net-plankton samples were collected by trolling a MTD net (XX13, mesh size of 100 μm) in the surface water around each stations. These samples mainly consisted of phytoplankton, such as diatoms and noctilucas with a small part of zooplankton and less particulate matter. Thus, net-plankton samples are referred to plankton samples in this paper. After removing excessive moisture by centrifuging, plankton samples were placed in glass bottles and frozen at −20°C until analysis.

Biological samples such as amphipods, mussels, ascidians, sea urchins, and several kinds of fish species were collected from three sampling stations, located at the entrance, middle, and bottom of the bay (Sts. A, B, and C in Figure 1), in September 1994 and May and August 1995 by scuba-diving or using a research bottom trawl. Details of these organisms are given in Table 1. After collecting, biological samples were placed in butyltin-free polyethylene bags and frozen at −20°C until analysis. The whole body or soft tissues of individuals were pooled and homogenized. In the case of some fish (such as conger-eel, greenling, and morid cod), representative tissues and organs were taken for chemical analysis.

Chemical Analysis

The analytical procedure for BTs was conducted following the methods described elsewhere (Harino and Fukushima 1992; Iwata *et al.* 1994) with slight modifications. Briefly, for seawater samples, 1-L of sea water acidified with 1 ml of 12 N HCl, were extracted with two 50-ml portions of 0.1% tropolone-benzene. After elimination of the moisture in the organic layer with anhydrous Na_2SO_4, the extract was concentrated nearly to dryness using a rotary evaporator (40°C) and made up to 5 ml with benzene. BTs in the extract were propylated by adding 5 ml of *n*-propyl magnesium bromide (ca. 2 mol L^{-1} in THF solution, Tokyo Kasei Kogyo Co. Ltd., Japan) as a Grignard reagent, and the mixture was shaken at 40°C for 1 h. After decomposition of the excess Grignard reagent with 20 ml of 1 N H_2SO_4, the derivatized extract was transferred to 20 ml of 10% benzene-hexane and concentrated nearly to dryness; the volume was made up to 5 ml with hexane. The extract was purified by eluting through a 6-g Florisil-packed wet column. The final hexane eluate from the cleanup column was concentrated to 5 ml and subjected to gaschromatophic quantification. For sediment samples, 5.0–10 g (wet wt) of sediment acidified with 5 ml of 2 N HCl was shaken with two 40-ml portions of 0.1% tropolone-acetone for 30 min. The sediment-solvent mixture was centrifuged at 3,000 rpm, and BTs in the supernatant were transferred to 0.1% tropolone-benzene. After elimination of the moisture in the organic layer with anhydrous Na_2SO_4, a procedure similar to that reported for sea water was followed. For biological samples, 1.0–3.0 g (wet wt) of tissue was homogenized with 70 ml of 0.1% tropolone-acetone and 5 ml of 2 N HCl. The homogenate was centrifuged at 3,000 rpm, and BTs in the supernatant were transferred to 0.1% tropolone-benzene. The following procedure was same as that for seawater and sediment.

Sample extracts were analyzed for BTs using capillary gas chromatography with flame photometoric detection (GC-FPD). Chromatographic separation was performed on a Hewlett-Packard 5890 Series II gas chromatograph with a 30 m × 0.25 mm (i.d.) DB-1 capillary column coated at 0.25 μm film thickness (J&W Scientific Co., Folsom CA, 100% dimethyl polysiloxane). The flame photometer was operated using a hydrogen-air-nitrogen flame and equipped with a 610-nm bandpass filter selective for tin-containing compounds.

Monobutyltin trichloride, dibutyltin dichloride, and tributyltin chloride of known amounts (0.1 μg each) spiked into the sea water and sediment from a less contaminated estuary and into the liver of Antarctic minke whale, which contained undetectable levels of BT residues, was concurrently run with samples through the whole analytical procedure for use as an external standard. Only freshly derivatized external standards prepared along with samples were used to estimate concentrations. Concentrations were quantified by comparing peak heights of each BT species in samples with those in the external standards. Procedural blanks were included with every batch of six samples to check for interfering compounds and to correct sample values, if necessary. Mono- and dibutyltin, probably originating from commercial solvents or reagents that came into contact with some plastic containing these compound, was found at trace levels in reagent

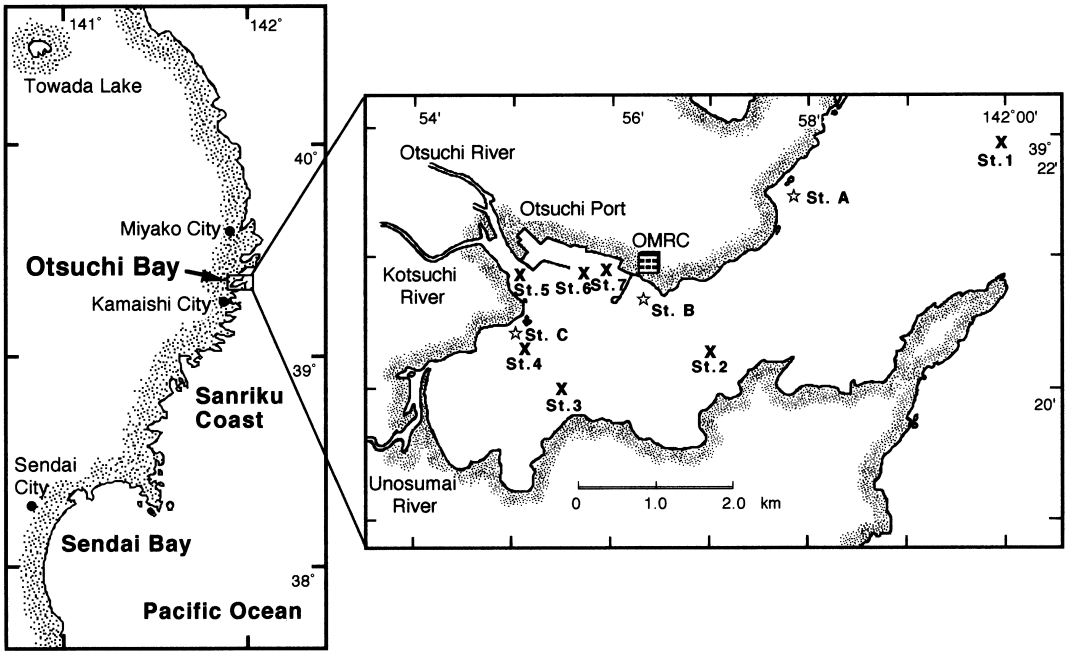

Fig. 1. Map showing sampling locations in Otsuchi Bay. OMRC indicates the location of Otsuchi Marine Research Center, Ocean Research Institute, University of Tokyo. Sea water samples were collected from Sts. 1 to 7 (shown as x). Sediment cores were collected from Sts. 2 and 4. Various marine organisms were collected at Sts. A, B, and C (shown as stars). Net-plankton samples were collected from Sts. 1 to 4, 6, and St. A

blanks. The values obtained for MBT and DBT in samples were therefore corrected for blank concentration. Detection limits of BTs in samples were assigned twice the values of procedural blanks.

Detection limits MBT, DBT, and TBT were; 8.0, 4.6, and 3.0 ng L^{-1} for seawater samples, 5.0, 1.0, and 1.0 ng g^{-1} (wet wt) for sediments, and 9.0, 1.0, and 1.0 ng g^{-1} (wet wt) for biological tissues, respectively. The average recovery rates through the whole analytical procedure for monobutyltin trichloride, dibutyltin dichloride, and tributyltin chloride dissolved and spiked into the various sample matrices were; 116 ± 20%, 93 ± 15%, and 99 ± 11% in the sea water (n = 5), 98 ± 14%, 126 ± 8%, and 109 ± 9% in the sediment (n = 4), and 104 ± 20%, 117 ± 14%, and 108 ± 5% for the biological tissues (n = 4), respectively. In addition, hexyl tributyltin was added as an internal standard in biological tissue and sediment samples, and its recoveries through the analytical procedure were more than 85%. All concentrations refer to BT species as the corresponding ion, and they were not corrected for the recovery of the internal standard.

Results and Discussion

Residue Levels and Distribution in Sea Water

BTs were detected in surface seawater samples collected from five stations in the bay (Figure 2). Total BT concentrations (ΣBT = MBT + DBT + MBT) in sea water were up to 27 ng L^{-1}, and higher levels were found at locations near harbor area of Otsuchi Port. With the increase in distance from the harbor area, BT concentrations in sea water decreased. BT residues in sea water from the middle of (St. 2) and outward from (St. 1) the bay were below the detectable levels. These trends suggest that maritime activities in the harbor have been a major source of BTs in this bay, and their emission rates from the source to open waters were slow. This may be attributable to a rapid degradation of these compounds in sea water (Stewart and de Mora 1990; Maguire 1996; Seligman *et al.* 1996) and/or absorption to suspended matters and subsequent scavenging to sediments (Harris *et al.* 1996; Batley 1996). Another possible explanation might be the exchange of water between inside and outside the bay (Shikama 1980) that facilitate the dilution of BTs in water column.

At four of five stations where BTs were detected, proportions of TBT were the highest among BT derivatives. Despite short half-life (from several days or weeks) of TBT in the water column (Stewart and de Mora 1990; Batley 1996; Maguire 1996; Seligman *et al.* 1996), great proportions of TBT suggests its continuous input, probably originating from illegal use as antifoulants, water discharge from harbor facilities, and/or desorption from polluted sediments (including paint chips) in the harbor area. Only at St. 3 were concentrations of DBT and MBT higher than those of TBT. Although the reason for this is still unclear, a coastal front formed around St. 3 by the input of fluvial discharge, where phytoplankton blooms were often observed (Wada *et al.* 1983), can be considered. Degradation of TBT in water is primarily a biotic process (Maguire 1996; Batley 1996; Seligman *et al.* 1996; Fent 1996) and, therefore, is likely to be accelerated by high biological activities. On the other hand, input of MBT and DBT, which can be derived from municipal and industrial wastewaters (Fent 1996), seems to be less because no intensive human/industrial activity can be found along Unosumai River and coastal areas proximal to St. 3.

Residue levels of TBT in sea water from Otsuchi Bay (<3.0–19 ng L^{-1}) were within the range of those values from various coastal areas of Japan (<3.0–30 ng L^{-1}) (Environment Agency Japan 1995) and lower than those in polluted areas such as Yokkaichi Port (10–25 ng L^{-1}) (Environment Agency Japan 1995) and Aburatsubo Bay (242 ± 30 ng L^{-1}) (Suzuki *et al.*

Table 1. Sample details of marine organisms collected from Otsuchi Bay

Species	n	Month and Year	Station[a]	Mean Length (mm)	Mean Weight (g wet wt)
Caprellids					
Caprella danilevskii	—	Sept. 1994	St. A	—	—
Caprella subinermis	—	Sept. 1994	St. A	—	—
Caprella equilibra	—	May 1995	St. B	—	—
Caprella mutica	—	May 1995	St. B	—	—
Caprella penantis S-type[b]	—	May 1995	St. B	—	—
C. penantis R-type[b] (male)	—	Aug. 1995	St. A	—	—
C. penantis R-type[b] (female)	—	Aug. 1995	St. A	—	—
Gammarid					
Jassa sp.	—	May 1995	St. B	—	—
Mussel					
Mytilus galloprovincialis	5	Sept. 1994	St. A	59	33.3[c]
Other organisms					
Ascidian, *Halocynthia roretzi*	3	Sept. 1994	St. C	58	52.3
Sea urchin 1, *Storongylocentrotus intermedius*	2	Sept. 1994	St. C	59	76.6[c]
Sea urchin 2, *S. intermedius*	3	Sept. 1994	St. A	53	70.8[c]
Fish					
Conger eel 1, *Conger myriaster*	1	Sept. 1994	St. A	735	650
Conger eel 2, *C. myriaster*	1	Aug. 1995	St. A	795	1,288
Conger eel 3, *C. myriaster*	1	Aug. 1995	St. C	366	155
Greenling, *Hexagrammos otakii*	1	Sept. 1994	St. A	240	260
Morid cod 1, *Physiculus maximowiczi*	1	Sept. 1994	St. A	180	73
Morid cod 2, *P. maximowiczi*	1	Aug. 1995	St. C	134	20.2
Gunnel 1, *Pholis nebulosa*	1	May 1995	St. B	102	7.5
Gunnel 2-1, *Pholis crassispina*	1	May 1995	St. B	185	17.4
Gunnel 2-2, *P. crassispina*	1	May 1995	St. B	125	6.6
Sculpin, *Pseudoblennius cottoides*	1	May 1995	St. B	114	23.3
Marine mammal					
Dall's porpoise,[d] *Phocoenoides dalli*	3	Feb. 1995	Off Sanriku	1,785	NM

NM, Not measured

[a] Sampling stations for these organisms shown in Figure 1

[b] *Caprella penantis* S- and R-type are the same types that Takeuchi (1995) refers to as *C. penantis* S- and R-type, respectively

[c] Soft tissue

[d] Data on adult males (n = 2) and a young female (n = 1) cited from Tanabe *et al.* (1998)

— Pooled sample

1998). Based on this information, butyltin contamination status of the Otsuchi Bay seemed to be rather similar to that in other parts of Japan. However, the residue levels near the harbor area can be considered to be toxic to susceptible organisms.

Vertical Profile in Sediment Cores

BT residues were detected in all layers of the sediment core samples. ΣBT concentrations in the cores from St. 2 and St. 4 were up to 260 and 86 ng g^{-1} (dry wt), respectively. Concentrations of TBT in the sediments from Otsuchi Bay (5.6–82 ng g^{-1} dry wt) were within the range of those values from various coastal areas of Japan (<3.0–440 ng g^{-1}) and lower than those in polluted areas such as Yokkaichi Port (70–240 ng g^{-1}) and Osaka Bay (120–440 ng g^{-1}) (Environment Agency Japan 1995).

Vertical profiles of BTs in the sediment cores from Sts. 2 and 4 are shown in Figure 3. A specific peak of residue levels was found in these profiles. Based on the result of lead isotope ^{210}Pb analysis, the sedimentary structure in these core samples appeared to be preserved, and a sedimentation rate of 0.36 and 0.17 cm/year were estimated at Sts. 2 and 4, respectively (data not shown). Hence, sedimentary date of the layer, which showed a peak of BT residues, can be estimated back to the early (at St. 2) or late (at St. 4) 1980s. The difference in the dates for maximum concentrations between St. 2 and St. 4 might have resulted from the spatial difference in BT deposition, sample collecting error when using the gravity corer, or physicochemical diffusion of BTs in the sediment. However, significant bioturbation was not observed in these core samples. It may be safe to assume that such vertical profiles of BTs in sediment cores suggest the peak period of usage in the 1980s and gradually decreased during the last decade.

Among BT derivatives, MBT was the predominant compound in sediments analyzed, followed by TBT and DBT (Figure 3). This pattern may result from their sorption onto particulate matters in the water column that finally settle and degrade in the sediments. Enrichment of MBT can be explained from the results in several studies (Randall and Weber 1986; Dowson *et al.* 1993a) that showed the strong sorption of MBT onto a representative mineral particle (hydrous iron oxide) under simulated estuarine conditions. Alternatively, rapid degradation of TBT to MBT in water column and/or surface sediment should be also considered (Seligman *et al.* 1996).

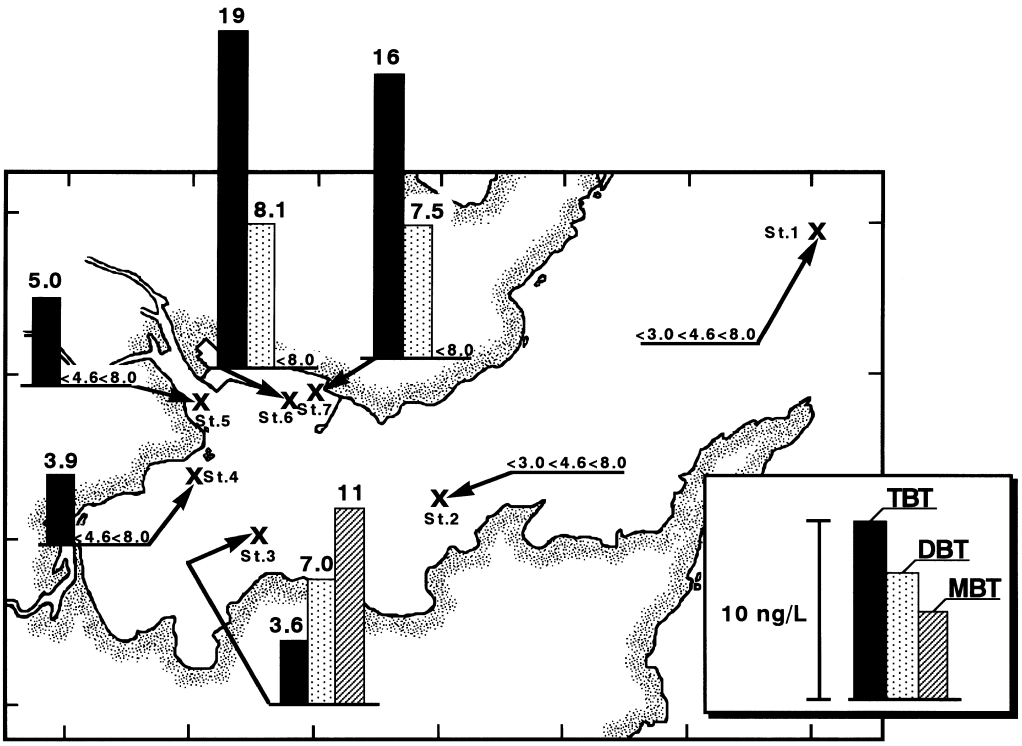

Fig. 2. Distribution of butyltin concentrations (ng L^{-1}) in surface sea water in Otsuchi Bay

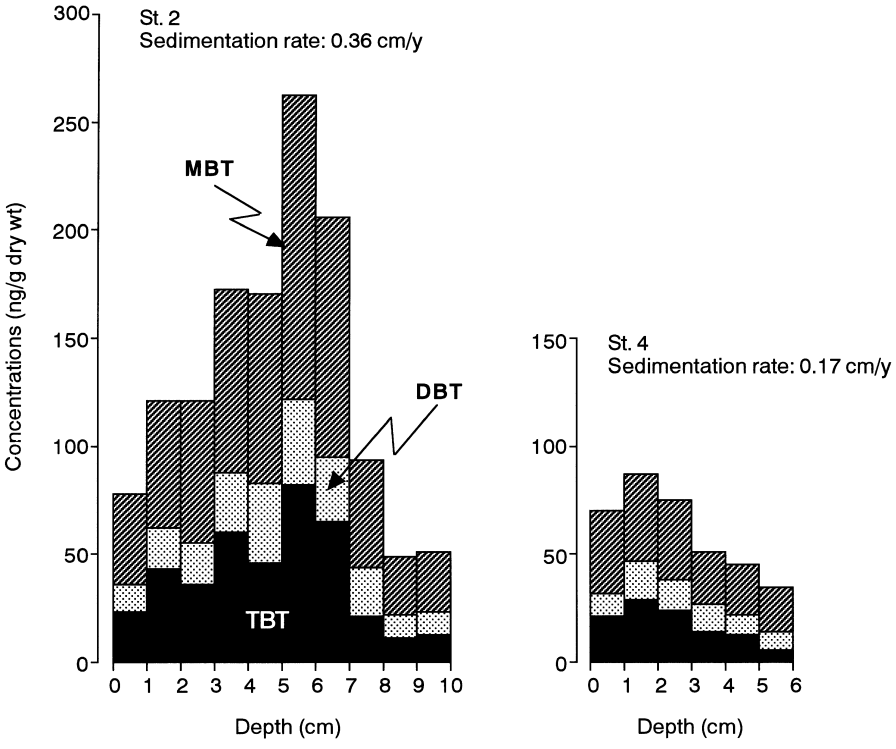

Fig. 3. Vertical profiles of butyltin residues in sediment cores of Otsuchi Bay

Another notable point in composition of BTs is the uniformity in the ratio of TBT to its breakdown products, DBT and MBT, at various depths (Figure 3). This may imply relatively slow degradation of these compounds in sediments. Several studies suggest slow degradation of TBT in marine and freshwater sediments with a half-life of up to a few years or even decades (Stewart and de Mora 1990; Dowson *et al.* 1993b; Maguire 1996; Batley 1996; Fent 1996), particularly in low water temperature areas (Adelman *et al.* 1990). The Otsuchi Bay is strongly influenced by the inflow of cold water of the

Oyashio Current and characterized by the low water temperatures (water temp. 5–10°C in winter and spring) (Shikama 1980; Kutsuwada 1990). Such conditions can cause slow degradation of BTs in the sediment. Stang and Seligman (1986) reported that MBT proportion of the ΣBT increased with core depth. Their study showed rapid degradation of TBT in sediments with half-lives in the range of several days (Stang *et al.* 1992). In contrast to these results, TBT and its breakdown products showed similar vertical profile in sediment cores from freshwater lakes (Fent 1996) and Arcachon harbor (Quevauviller *et al.* 1994), which indicates the slow degradation and persistent nature of TBT. Probably, such contradictory trends reported among various studies may have resulted from different environmental conditions, such as water temperature and sediment characteristics.

Residue Levels and Distribution in Biota

BT residues were detected in all biological samples analyzed (Table 2). Accumulation of these compounds has also been found in the liver of Dall's porpoises collected near Otsuchi Bay (off Sanriku) (Tanabe *et al.* 1998). These observations indicate the expansion of contamination in the marine ecosystem. BT concentrations in almost all organisms, except for plankton, caprellids, and gunnels, were in sub μg/g or a few ng/g levels (Table 2). These concentrations were lower than those reported in fish and shellfish from Tokyo Bay (Higashiyama *et al.* 1991; Takayama *et al.* 1995; Environment Agency Japan 1995). BT concentrations in the liver of Dall's porpoises seemed to be rather high (300–1,000 ng g^{-1} wet wt), however, their levels were significantly lower than those found in finless porpoises from Seto-Inland Sea (∼10 μg/g) and Nagasaki (∼5 μg/g) that were affected by intensive human activities (Tanabe *et al.* 1998). Despite lower magnitude of the contamination in Otsuchi Bay, TBT concentrations in some organisms (such as caprellids) exceeded its no observed effect levels reported for susceptible organisms (Bryan and Gibbs 1991; Gibbs and Bryan 1996; Alzieu 1996).

Among various biota samples analyzed, plankton showed the highest concentrations: up to 1,700 ng ΣBT g^{-1} (wet wt). Spatial distribution of BT concentrations in plankton were approximately similar to those in sea water: higher residue levels were found in the harbor area of Otsuchi Port (Figure 4). BTs were also detected in the samples from middle (St. 2) and outward (St. 1) of the bay, where BTs were not detected in sea water. In samples collected from St. 3–6, TBT were accumulated up to ∼70,000 times to that in sea water. These results suggest high accumulation of BTs in plankton. Among BT derivatives, TBT was the predominant compound in plankton samples, and its proportion to ΣBT were higher than those found in sea water. This indicates the preferential accumulation of TBT in plankton. It may be due to the higher hydrophobicity of TBT with higher K_{ow} than DBT and MBT (Poerschmann *et al.* 1998). In addition, the enrichment of TBT in the surface microlayer, where the organic matter such as oils are concentrated, has been observed (Batley *et al.* 1996). Furthermore, the predominance of TBT in plankton suggests the continuous fresh input of TBT into the environment because the half-lives in phytoplankton were several days (Maguire *et al.* 1984; Lee *et al.* 1989). Some species of phyto- and zooplankton are susceptible to TBT at a few μg L^{-1} or even lower concentrations (Bryan and Gibbs 1991; Fent 1996; Alzieu 1996). Hence, such accumulative properties in the plankton as well as the continuous input of TBT may pose a higher risk to their survival, which can be a cause of disturbance in the natural ecosystem.

Followed by plankton, relatively high concentrations were found in caprellids (79–180 ng g^{-1} wet wt) and several species of smaller fish such as gunnels (∼260 ng g^{-1} wet wt). Caprellids collected from the entrance of the Bay (St. A) showed lower residue levels than those from the middle (St. B) of the bay ($p < 0.05$ by Mann-Whitney U test). It may agree with the distribution of BTs in sea water and plankton observed. Such distributions were not reflected in fish species such as conger eels and morid cods, probably due to their migration.

Bioaccumulation Profiles in Marine Ecosystem

To elucidate the bioaccumulation profiles of BTs in the marine ecosystem, the residue levels of BTs were compared among different compartment of the ecosystem. ΣBT concentrations in sea water, sediment, plankton, primary consumers (filter-feeding benthic organisms including caprellids, gammarids, mussels, ascidians, and sea urchins), smaller fish (gunnels and sculpins feeding mainly zooplankton and small crustaceans), larger fish (conger-eels, greenlings, and morid cods showing a carnivorous habit), and marine mammal (Dall's porpoises) (data cited from Tanabe *et al.* 1998) are shown in Figure 5. Data for sea water and plankton samples from the stations near the harbor area (St. 6 and 7) were excluded from this comparison. Data for fish and shellfish include only those concentrations in the whole-homogenized soft tissues or muscle that contain greater burden of BT residues among the tissues (Takahashi *et al.* 1997). ΣBT concentrations in the whole body of Dall's porpoises (41–120 ng g^{-1}) were estimated from their hepatic concentrations based on the information of BT burden percentages in each tissues and organs of finless porpoises (Iwata *et al.* 1995). Caprellids, especially the genus *Caprella*, are usually regarded as benthic species and primary consumers (Caine 1980), which were confirmed by the successful rearing of several species of *Caprella* using only diatoms as food (Takeuchi 1989; Takeuchi and Hirano 1991, 1992). The caprellid and gammarid amphipods are also considered to be one of the most important prey items for the smaller fish (<13 cm in body length) inhabiting shallow-water ecosystem (Hirayama 1978; Caine 1989; Takeuchi 1989). Although conger eels, greenlings, and morid cods cannot be considered as prey items for Dall's porpoises, which feed mainly on mesopelagic myctophids and squids (Ohizumi 1998), the concentrations of TBT in these fish were almost similar to those found in squid livers in the Northwest Pacific off Sanriku (17–280 ng g^{-1} wet wt) (Yamada *et al.* 1997). Furthermore, the Otsuchi Bay environment favorably connects to the Pacific waters in view of its wide and deep entrance. Thus, the comparison of the residue levels among these organisms can reflect the BT profile of the marine ecosystem in the Pacific coast of northern Japan.

As shown in Figure 5, BTs were obviously accumulated in most of these organisms up to ∼50,000 times higher than in sea water. However, there were no significant differences in the BT residue levels between the trophic levels. This means that no considerable biomagnification for these compounds was observed through the food chain. It is quite different from the case of persistent organochlorines, such as PCBs and DDTs, that are

Table 2. Butyltin concentrations (ng g^{-1} wet wt) in marine organisms collected from Otsuchi Bay

Sample	Station[a]	Tissue/Organ[b]	MBT	DBT	TBT	ΣBT[c]
Caprellids						
Caprella danilevskii	St. A	W	11	9.2	59	79
Caprella subinermis	St. A	W	17	15	57	89
Caprella equilibra	St. B	W	28	13	71	110
Caprella mutica	St. B	W	19	13	94	130
Caprella penantis S-type[d]	St. B	W	24	17	140	180
C. penantis R-type[d] (male)	St. A	W	11	8.7	58	78
C. penantis R-type[d] (female)	St. A	W	17	7.9	73	98
Gammarid						
Jassa sp.	St. B	W	25	9.5	12	47
Mussel						
Mytilus galloprovincialis	St. A	S	9.4	34	45	88
Other organisms						
Ascidian, *Halocynthia roretzi*	St. C	W	<9.0	13	42	55
Sea urchin 1, *Strongylocentrotus intermedius*	St. C	S	<9.0	11	41	52
Sea urchin 2, *S. intermedius*	St. A	S	<9.0	5.4	17	22
Fish						
Conger eel 1, *Conger myriaster*	St. A	M	21	13	13	47
Conger eel 2, *C. myriaster*	St. A	M	<9.0	5.3	9.2	15
Conger eel 2, *C. myriaster*	St. A	L	66	60	28	150
Conger eel 3, *C. myriaster*	St. C	W	<9.0	8.6	14	23
Greenling, *Hexagrammos otakii*	St. A	M	12	2.1	4.2	18
Morid cod 1, *Physiculus maximowiczi*	St. A	M	25	5.1	4.2	34
Morid cod 1, *P. maximowiczi*	St. A	L	<9.0	11	8.5	20
Morid cod 1, *P. maximowiczi*	St. A	G	12	4.6	9.9	27
Morid cod 2, *P. maximowiczi*	St. C	W	<9.0	1.8	5.1	6.9
Gunnel 1, *Pholis neblosa*	St. B	W	<9.0	6.1	31	37
Gunnel 2-1, *Pholis crassispina*	St. B	W	11	8.8	61	81
Gunnel 2-2, *P. crassispina*	St. B	W	15	32	210	260
Sculpin, *Pseudoblennius cottoides*	St. B	W	<9.0	7.3	79	86
Marine mammal						
Dall's porpoise,[e] *Phocoenoides dalli*	Off Sanriku	L	97 (50–120)	430 (180–600)	230 (110–310)	760 (340–1,000)

Figures in parentheses indicate the range of concentrations

[a] Sampling stations shown in Figure 1

[b] Tissue/organs were shown as: M (muscle), L (liver), G (gill), S (whole soft tissue), and W (whole body)

[c] ΣBT = MBT + DBT + TBT

[d] *Caprella penantis* S- and R-type are the same types that Takeuchi (1995) refers to as *C. penantis* S- and R-type, respectively

[e] Data cited from Tanabe *et al.* (1998)

well known for their significant biomagnification and much higher levels in marine mammals (Tanabe *et al.* 1984; Tanabe and Tatsukawa 1991). Biodegradable nature (Kimmel *et al.* 1977; Fent 1996; Lee 1996) and low assimilative properties (Yamada *et al.* 1994) of BTs might be attributable to their lower food chain transfer. Such bioaccumulation profiles in the marine food chain can partly be supported by some observations showing less biomagnification trends for these compounds in prey-predator relationships (Bryan and Gibbs 1991; Iwata *et al.* 1995; Kim *et al.* 1996a, 1996b; Guruge *et al.* 1996; Kannan *et al.* 1997; Takahashi *et al.* 1997). A recent study also reported that the biomagnification of TBT was not likely to occur in the foodweb of a freshwater lake (Stäb *et al.* 1996). To our knowledge, this is the first integrative presentation of the accumulation profile of BTs in the various compartments of marine ecosystem including higher trophic mammals that showed no considerable biomagnification through the food chain.

Relatively high concentrations were found in caprellids and their predators, gunnels. It suggests species-specific accumulation of these compounds. To compare such species-specific trends between various organisms, bioconcentration factors (BCFs) for TBT in the marine organisms analyzed in this study were roughly estimated based on the ratio of the concentration in whole body of animals to seawater (mean, 4.2 ng L^{-1}) (Table 3). BCFs obtained from the field data could be somewhat higher than those measured from laboratory experiments due to the portion of uptake via food. Nevertheless, as compared among these organisms, BCFs for TBT in conger eels, gammarids, and mussels were within the range of those data in fish, amphipods, and mollusks reported in various field and laboratory studies, respectively (Table 3). Whereas, those values in gunnels and caprellids were higher than in other species. It suggests that these organisms tend to accumulate TBT at higher levels than the other species, and great bioaccumulation of BTs in these organisms may have implications for their survival.

Why does BT accumulation pose such a species-specific trend? One plausible explanation may be given from the viewpoint of differences in metabolic capacity among organisms. The composition of BTs in the marine organisms from

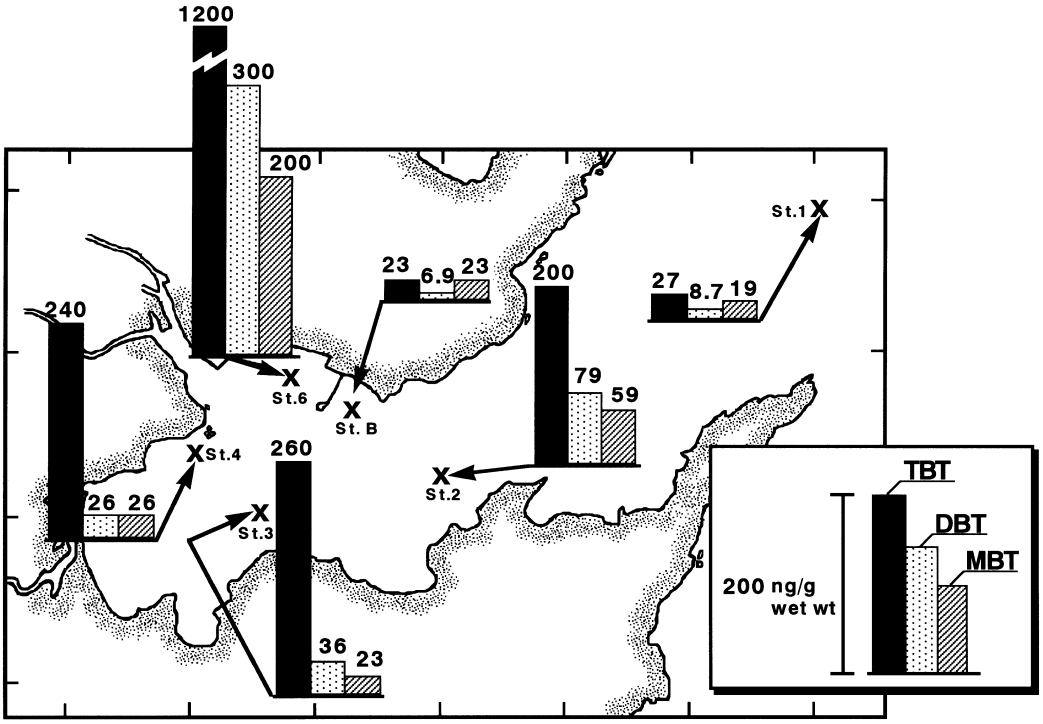

Fig. 4. Distribution of butyltin concentrations (ng g^{-1} wet wt) in plankton in Otsuchi Bay

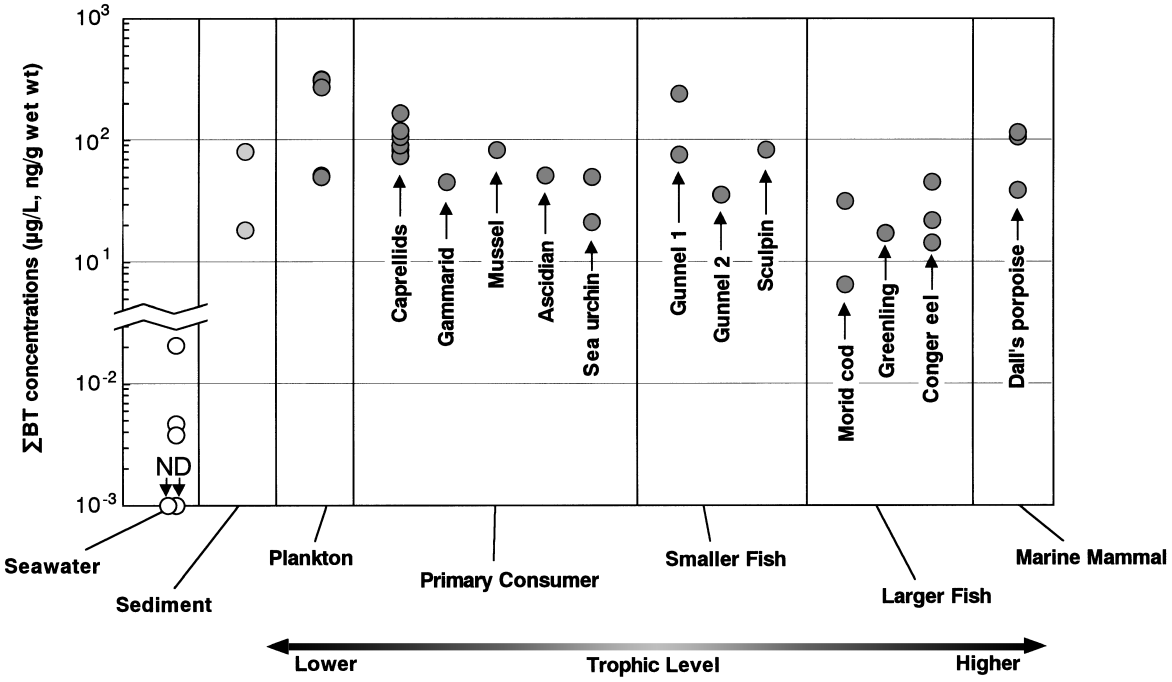

Fig. 5. Accumulation profile of butyltin residues in the Otsuchi Bay ecosystem. Common names used in this figure such as caprellids, gammarids, mussels, ascidians, sea urchins, gunnels 1 and 2, sculpins, morid cods, greenlings, conger eels, and Dall's porpoises indicate those species shown in Table 1. Data of ΣBT concentrations for fish and shellfish shown in this figure were based on those in the whole-homogenized soft tissues or muscle. Whole body basis concentrations of ΣBT in Dall's porpoises shown in this figure were estimated by the manner explained in the text

Otsuchi Bay is shown in Figure 6. Among BT derivatives, TBT residues were more predominant than its metabolites in some of the lower trophic animals including caprellids and gunnels, that showed higher residue levels with higher BCF values than the other species. Particularly, caprellids accumulated BTs with significant high portion of TBT compared to those in gammarids whose habitat and trophic level in the ecosystem are similar to those of caprellids. It can be considered that

Table 3. Bioconcentration factors (BCFs) for TBT in aquatic organisms

Species	BCF[a]	Reference
Fish		
Sheepshead minnow, *Cyprinodon variegatus*	2,600	Ward *et al.* 1981
Rainbow trout, *Salmo gairdneri*	410	Martin *et al.* 1989
Guppy, *Lebistes teticulatus*	240–460	Tsuda *et al.* 1990
Minnow (larvae), *Phoxinus phoxinus*	410–540	Fent 1991
Goldfish, *Carassius auratus*	2,000	Tsuda *et al.* 1991
Mullet, *Mugil cephalus*	2,300–3,000	Yamada *et al.* 1992
Filefish, *Rudarius ercodes*	3,200–3,600	Yamada *et al.* 1992
Red sea bream, *Pagrus major*	9,400–11,000	Yamada *et al.* 1992
Grayling (larvae), *Thymallus thymallus*	2,000	Fent and Looser 1995
Morid cod, *Physiculus maximowiczi*	1,200	This study
Conger eel, *Conger myriaster*	3,300	This study
Gunnels, *Pholis crassispina*	19,000–50,000	This study
Amphipods		
Gammarid, *Rhepoxynius abronius*	360[b]	Meador *et al.* 1993
Gammarid, *Eohaustorius estuarius*	6,300[b]	Meador *et al.* 1993
Gammarid, *Jassa* sp.	2,700	This study
Caprellid[c]	14,000–33,000	This study
Mollusks		
Blue mussel, *Mytilus edulis*	1,500–7,300	Laughlin and French 1988
Blue mussel, *M. edulis*	7,000–19,000	Zuolian and Jensen 1989
Blue mussel, *M. edulis*	10,000	Suzuki *et al.* 1998
Mussel, *Mytilus graynus*	11,000	Suzuki *et al.* 1998
Mussel, *Mytilus galloprovincialis*	11,000	This study
Oyster, *Crassostrea gigas*	2,000–6,000	Waldock *et al.* 1983
Oyster, *Ostreas edulis*	1,000–1,500	Waldock *et al.* 1983
Oyster, *Crassostrea gigas*	16,000	Waldock *et al.* 1987
Gmelin, *Nucella lima*	2,200–2,900	Stickle *et al.* 1990
Dog-whelk, *Nucella lapillus*	29,000**	Bryan and Gibbs 1991
Rock shell, *Thais clavigera*	5,000–10,000	Horiguchi *et al.* 1995
Soft-shelled clam, *Mya arenaria*	5,700–220,000	Kure and Depledge 1994

[a] Values rounded to two-figure number for the comparison
[b] BCFs estimated with the assumption of 80% of moisture content in the tissue of organisms
[c] Minimum BCF in *Caprella subinermis* to maximum in *Caprella penantis* S-type

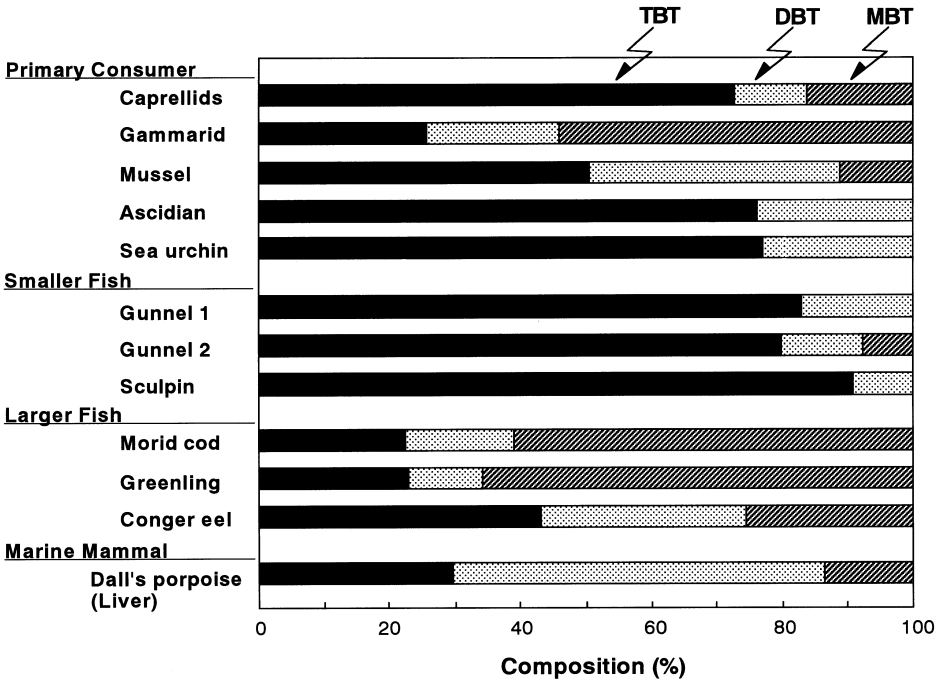

Fig. 6. Butyltin compositions in the whole-homogenized soft tissues or muscle of various marine organisms from Otsuchi Bay and in the liver of Dall's porpoises cited from Tanabe *et al.* (1998). Common names used in this figure such as caprellids, gammarids, mussels, ascidians, sea urchins, gunnels 1 and 2, sculpins, morid cods, greenlings, conger eels, and Dall's porpoises indicate those species shown in Table 1

caprellids (and also gunnels) may have a lower metabolic capacity to degrade TBT and therefore may accumulate BTs at elevated concentrations. These results suggest that certain organisms in the food chain, which have a low capacity to degrade TBT, may accumulate BTs at higher concentrations than the other species.

To our knowledge, this is the first report describing the comprehensive accumulation profile of BTs in an entire marine ecosystem with various trophic organisms. Among organisms examined, caprellids and gunnels were found to be at higher risk from BT contamination than the other species, and thus, it can be a break point for the disturbance in the natural food chain structure. Lee (1986, 1996) suggested that susceptibility of mollusks to TBT may be connected to their low detoxifying activity due to low cytochrome P-450 content and mixed-function oxygenase activity that has been reported to play a role as a major function for TBT metabolism. A similar feature is expected for the other organisms, such as caprellids; however, the implications of species-specific accumulation and toxic effects of organotins is yet to be understood. Further studies are required on this topic.

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