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Bioaccumulation of tributyltin and triphenyltin compounds through the food web in deep offshore water

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Abstract—Concentrations of tributyltin (TBT) and triphenyltin (TPT) compounds were determined in bottom seawater, sediments, and organisms of various trophic levels in the marine benthic food web in the Sea of Japan to clarify how the bioaccumulation patterns of TBT and TPT in the deep-sea ecosystem differ. TBT was detected in all samples: 0.3–0.8 ng/l in bottom seawater, 4.4–16 ng/g dry wt in sediment, and 1.8–240 ng/g dry wt in various organisms. TBT and TPT concentrations were lower in bottom seawater than in shallower coastal waters. The TPT concentration in bottom seawater was less than our detection limit (0.9 ng/l), but it was 3.9–12 ng/g dry wt in sediment and 5.0–460 ng/g dry wt in organisms. TPT concentrations in deep-sea sediments and organisms were similar to those in coastal areas and higher in organisms at higher trophic levels, suggesting that TPT bioaccumulates through the food web. However, no such trend was observed for TBT. A laboratory rearing experiment demonstrated that sediment-sorbed TBT and TPT can be transferred to polychaetes. We conclude that TPT can be transferred to benthic organisms from sediments and then bioaccumulate through the food web. Sediments can thus act as a secondary source of TPT.

Key words: bioaccumulation, tributyltin, triphenyltin, food web, deep offshore, laboratory experiment, polychaetes

Introduction

Aquatic organisms, such as fish, bioaccumulate contaminants through two main pathways: direct uptake from the water across the gills (bioconcentration) and dietary uptake (biomagnification). Information on dietary uptake is necessary for a better understanding of bioaccumulation through the food web in aquatic ecosystems. Persistent organic pollutants, such as polychlorinated biphenyls, are known to bioaccumulate through the food web (Tanabe et al. 1984). However, tributyltin (TBT) appears to be an exception and does not bioaccumulate through the food web (Stab et al. 1996, Takahashi et al. 1999). Little is known about the bioaccumulation of triphenyltin (TPT) through the food web, but it has been documented in a shallow freshwater lake in the Netherlands (Stab et al. 1996). TBT concentrations in deep-sea fish are comparable to levels in coastal-dwelling fish (Borghi and Porte 2002); in contrast, deep-sea fish contain much higher levels of TPT than coastal fish. In spite of these findings, few studies have investigated the bioaccumulation of TBT and TPT in deep-sea ecosystems.

Hazardous hydrophobic chemicals that enter marine environments are generally adsorbed onto suspended substances and finally deposited in sediments (Tanabe and Tatsukawa 1981, Yamada 1994). The TBT concentration in sediment is 300–50,000 times that in seawater in Aburatsubo Bay, Japan (Yamada 1999). Although the use of organotin compounds (OTs), such as TBT and TPT, in antifouling paints has been regulated in Japan since 1990, concentrations of TBT and TPT in sediment were 47–300 and 1.3–15 ng/g dry wt, respectively, in Tokyo Bay in 1999 (Ministry of the Environment 2000), which suggests that OTs discharged in the past remain in sediments. Is it possible that OTs in sediments are taken up by benthic organisms and then bioaccumulate through the food web? If so, sediments might act as a secondary source of OT pollution, especially in deep offshore waters where OT concentrations are generally lower than in coastal waters.

This study was conducted to determine whether TBT and TPT bioaccumulate through the food web in deep offshore waters of the Sea of Japan and how bioaccumulation patterns of TBT and TPT differ in the deep-sea ecosystem (Ikeda et al. 2002). We also conducted a laboratory rearing experiment to investigate the transfer of sediment-sorbed TBT and TPT from environmentally contaminated marine sediment to an infaunal surface deposit-feeding polychaete, *Perinereis nuntia*.

Materials and Methods

Bottom seawater was collected at St. 1 (350–400-m depth) and St. 2 (115-m depth); sediments were collected at St. 1, St. 2, and St. 3; and aquatic organisms were collected in deep water off the San-in coast (A) and over the Yamato Bank (B) during 1998 and 1999 (Fig. 1). TBT and TPT were analyzed in seawater essentially as described by Harino and Fukushima (1992) and in sediments and organisms as described by Takami et al. (1988). To determine the trophic levels of organisms, we analyzed the frequency of prey organisms in the stomachs of predators collected in waters off the San-in coast and over the Yamato Bank. We then clarified the bioaccumulation patterns of TBT and TPT according to the relationships between TBT or TPT concentrations in organisms and the organisms' trophic levels.

In the laboratory rearing experiment, polychaetes were reared for 56 d in marine sediment containing TBT and TPT. Each day, trace amounts of formula feed were supplied to the sediment surface to induce polychaetes to feed. The polychaetes ingested sediment particles together with the feed. TBT and TPT were analyzed essentially as described by Ministry of the Environment (1999, 2001). We calculated the ratio of the contaminant concentration in polychaetes to that in sediment for TBT and TPT on the basis of the concentrations at the end of the 56-d experiment.

The TBT or TPT concentration was shown as TBT+ or TPT+ concentration, respectively in the data from the field determination and the laboratory experiment.

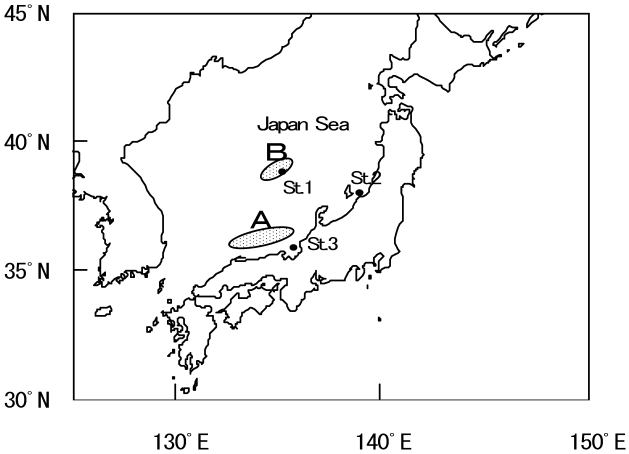

Fig. 1. Locations of sampling stations for bottom seawater, sediments, and organisms (A, off the San-in coast; B, over the Yamato Bank).

Results and Discussion

TBT and TPT concentrations in bottom seawater and deep-water sediments of the Sea of Japan

The TBT concentration in bottom seawater was 0.6 and 0.8 ng/l at St. 1 and 0.3 and 0.6 ng/l at St. 2. The TPT concentration in bottom seawater was below the detection limit of 0.9 ng/l at both stations. These values are similar to those previously reported for offshore waters, where OT concentrations are lower than in coastal waters (Yamada et al. 1997). The TBT concentrations in sediment collected at St. 1, St. 2, and St. 3 were 5.6 and 16, 4.4 and 5.6, and 5.9 and 8.3 ng/g dry wt, respectively, whereas the TPT concentrations were 3.9 and 6.7, 5.9 and 7.4, and 6.1 and 12 ng/g dry wt, respectively. The concentrations did not differ among these stations. Although the sediment TBT concentrations at these stations were lower than those reported for Tokyo Bay (47–300 ng/g dry wt), the sediment TPT concentrations were similar for both marine areas (1.3–15 ng/g dry wt) in 1999 (Ministry of the Environment 2000). Sediment TBT and TPT concentrations were 7500–26,000 times and >4300 times, respectively, their concentration in seawater at St. 1. These high sediment concentrations suggest that TBT and TPT in sediment may be the main secondary source of TBT and TPT pollution in deep waters of the Sea of Japan.

The food-chain structure in deep waters off the San-in coast and over the Yamato Bank

To determine the food-chain structure, we classified the prey organisms in the stomachs of predators collected in deep water off the San-in coast (Table 1) into three trophic levels:

Trophic level 1: organisms ingesting mainly detritus

Trophic level 2: organisms ingesting Polychaeta, Amphipoda, Euphausiacea, or Ophiuroidae

Trophic level 3: organisms ingesting fish, decapods, and squid

According to this analysis, we classified *Eualus biunguis*, *Pandalus eous*, and *Argis toyamaensis* into trophic level 1; *Bothrocara hollandi*, *Arctoscopus japonicus*, *Glyptocephalus stelleri*, and *Chionoecetes opilio* into trophic level 2; and *Hippoglossoides dubius*, *Malacocottus gibber*, *Petroschmidtia toyamensis*, and *Lycodes tanakae* into trophic level 3. From these findings, we determined the food-chain structure for deep-water organisms off the San-in coast (Fig. 2).

To determine the food-chain structure, we also classified the prey organisms in the stomachs of predators collected in deep water over the Yamato Bank (Table 2) into the same

Table 1. Frequencies of prey taxa in the stomachs of predators collected in deep water off the San-in coast (A in Fig. 1).

Predator	Frequency (%)[a]								
	Fish	Squid	Decapods	Amphipoda	Euphausiacea	Polychaeta	Ophiuroidae	Shellfish	Detritus
Lycodes tanakae	27	23	27	27				17	
Petroschmidtia toyamensis	17	3.3	17	6.7	3.3	13	6.7	50	
Malacocottus gibber	6.7	6.7	30	50	17	6.7	3.3	27	
Hippoglossoides dubius	6.7	33	13	3.3	17			3.3	
Chionoecetes opilio			13	13		3.3	3.3	3.3	
Glyptocephalus stelleri				6.7		50	23	6.7	
Arctoscopus japonicus				87	13				
Bothrocara hollandi			17	67	6.7	3.3	3.3		
Argis toyamaensis			3.3	13			3.3	17	100
Pandalus eous			13	17		17	6.7	6.7	100
Eualus biunguis								6.7	100

[a] (number of predators ingesting the prey/total number of predators examined [30 individuals])×100

Table 2. Frequencies of prey taxa in the stomachs of predators collected in deep water over the Yamato Bank (B in Fig. 1).

Predator	Frequency (%)[a]								
	Fish	Squid	Decapods	Amphipoda	Euphausiacea	Polychaeta	Ophiuroidae	Shellfish	Detritus
Bathyraja smirnovi	13	17	27	93	13				
Hippoglossoides dubius	6.6	3.3	17	3.3	3.3	3.3	87	3.3	
Malacocottus gibber	10	6.6	40	57	33	13	3.3	10	
Berryteutis magister	30	17	6.6	40	10				50
Chionoecetes opilio			3.3	13		3.3	3.3	3.3	100
Glyptocephalus stelleri	3.3			3.3		50	23		
Arctoscopus japonicus				90	10				
Bothrocara hollandi	6.6		17	77	13	3.3	3.3		
Careproctus trachysoma			6.6	93	67				
Enoploteuthis chunii				73	40				
Argis toyamaensis			3.3	10			3.3	10	100
Pandalus eous			3.3	3.3		13	6.6	6.6	100
Lebbeus longipes								6.6	100

[a] (number of predators ingesting the prey/total number of predators examined [30 individuals])×100

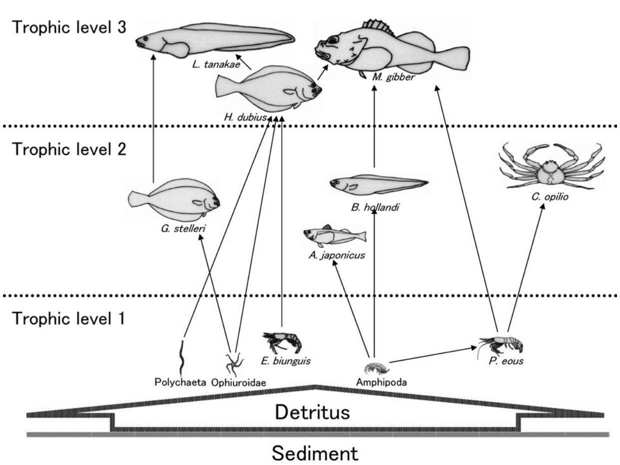

Fig. 2. Food-chain structure of deep-water organisms off the San-in coast (A, Fig. 1).

three trophic levels: *Lebbeus longipes*, *P. eous*, and *A. toyamaensis* into trophic level 1; *B. hollandi*, *A. japonicus*, *G. stelleri*, and *C. opilio* into trophic level 2, and *Berryteutis magister* (in this species, the detritus in the stomach was not organic matter from the sediment surface but crushed prey organisms), *M. gibber*, *H. dubius*, and *Bathyraja smirnovi* into trophic level 3. From these findings, we determined the food-chain structure for the deep-water organisms over the Yamato Bank (Fig. 3).

TBT and TPT concentrations in organisms collected in the deep waters of the Sea of Japan

The average TBT concentration in each organisms off the San-in coast ranged from 4.6 ng/g dry wt (2.5 ng/g wet wt) in Ophiuroidae to 210 ng/g dry wt (60 ng/g wet wt) in *A. japonicus* (Fig. 4), and over the Yamato Bank ranged from

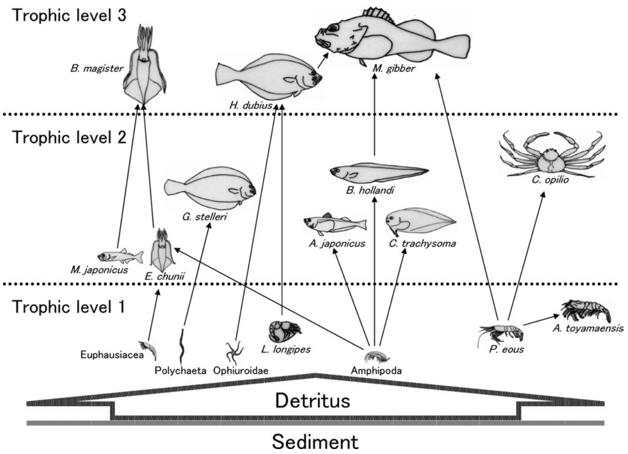

Fig. 3. Food-chain structure of deep-water organisms over the Yamato Bank (B, Fig. 1).

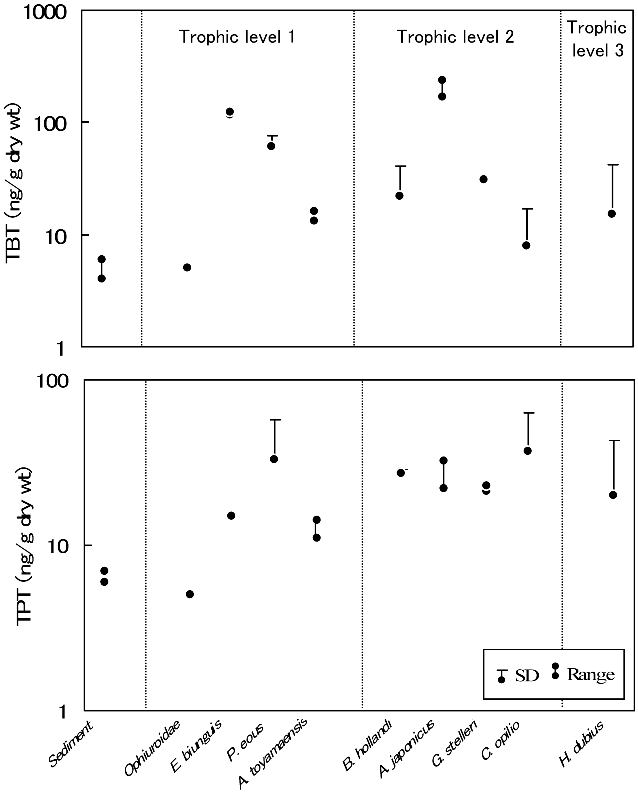

Fig. 4. Relationships between tributyltin (TBT) and triphenyltin (TPT) concentrations in organisms and their trophic levels in the deep-water food chain off the San-in coast (A , Fig. 1).

3.6 ng/g dry wt (1.0 ng/g wet wt) in *C. opilio* to 170 ng/g dry wt (42 ng/g wet wt) in *A. japonicus* (Fig. 5). These values are similar to those reported for mesopelagic myctophids (<5.0–35 ng/g wet wt) collected from the western North Pacific (Takahashi et al. 2000).

The average TPT concentration in each organisms off the San-in coast ranged from 5.0 ng/g dry wt (2.7 ng/g wet wt) in Ophiuroidae to 37 ng/g dry wt (8.1 ng/g wet wt) in *C. opilio* (Fig. 4), and over the Yamato Bank ranged from

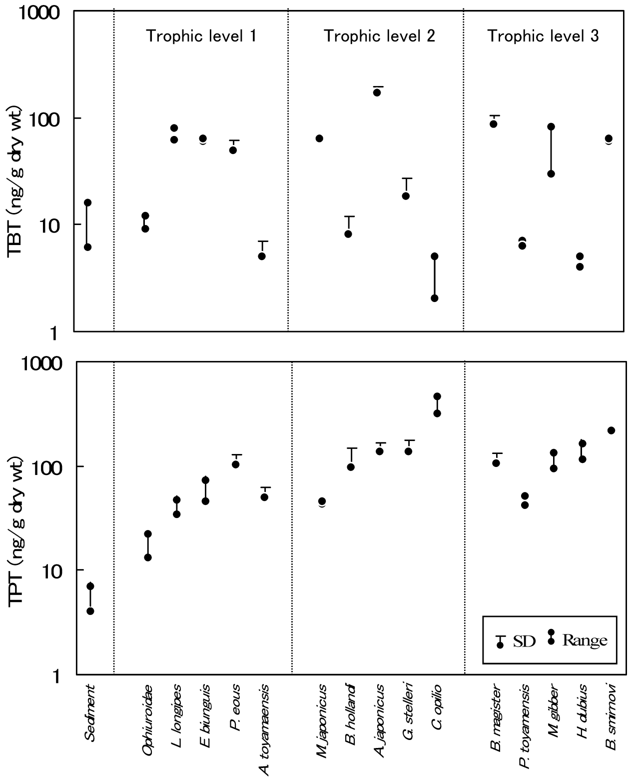

Fig. 5. Relationships between TBT and TPT concentrations in organisms and their trophic levels in the deep-water food chain over the Yamato Bank (B, Fig. 1).

18 ng/g dry wt (9.5 ng/g wet wt) in Ophiuroidae to 390 ng/g dry wt (72 ng/g wet wt) in *C. opilio* (Fig. 5). These values are similar to those reported in sea bass (<20 ng/g wet wt) collected from Tokyo Bay in 1999 (Ministry of the Environment 2000). The TPT concentration did not differ between the deep offshore water and the shallow waters of Tokyo Bay.

TPT concentrations in deep-water organisms at trophic levels 2 and 3 were higher than those in organisms at trophic level 1, both off the San-in coast and over the Yamato Bank. TPT concentrations in trophic level 1 organisms collected over the Yamato Bank were higher than those in trophic level 1 organisms from off the San-in coast. Similarly, TPT concentrations in organisms at trophic levels 2 and 3 collected over the Yamato Bank were higher than those in organisms at those trophic levels from off the San-in coast. These results suggest that the TPT concentrations in organisms at trophic levels 2 and 3 reflect those in organisms at trophic level 1.

Direct uptake from water versus dietary uptake

OTs bioaccumulate mainly through two pathways: direct uptake from water across the gills and dietary uptake (Yamada et al. 1994). We estimated the contribution of direct uptake to TBT and TPT concentrations in organisms over the Yamato Bank by using equation 1:

$$\text{Contribution of direct uptake} = \frac{\text{Concentration in seawater (ng/l)} \times BCF}{\text{Concentration in organisms (ng/g dry wt)} \times (1-WC)} \quad (1)$$

where BCF is the bioconcentration factor which is calculated as a ratio of concentration in organisms to that in seawater and WC is the water content of the organisms. TBT and TPT concentrations in seawater used in the calculation were 0.7 ng/l (the average TBT concentration over the Yamato Bank) and 0.45 ng/l (half the TPT detection limit of 0.9 ng/l), respectively. For organisms over the Yamato Bank, previously determined BCF values for TBT and TPT in marine fish (5000 and 3500, respectively; Yamada and Takayanagi 1992) and shrimp (5500 and 200, respectively; Hori et al. 2002) and the average WC of marine fish and shrimp (0.80 and 0.74 g/g wet wt, respectively) over the Yamato Bank were used in the calculation.

The contribution of direct uptake to the TBT concentration in organisms thus ranged from 0.1 (*A. japonicus*) to 3.6 (*H. dubius*) in fish and from 0.2 (*L. longipes*) to 3.0 (*A. toyamaensis*) in shrimp. On the other hand, the contribution of direct uptake to the TPT concentration ranged from 0.06 (*H. dubius*) to 0.18 (*P. toyamensis*) in fish and from 0.003 (*P. eous*) to 0.006 (*L. longipes*) in shrimp. Thus, direct uptake of TPT was less than that of TBT in these organisms. These results suggest that direct uptake is less important than dietary uptake for bioaccumulation of TPT by organisms inhabiting the deep water over the Yamato Bank.

Relationship between TBT and TPT concentrations in organisms and trophic level

The TPT concentration was higher in deep-water organisms at higher trophic levels from both off the San-in coast (Fig. 4) and over the Yamato Bank (Fig. 5), suggesting that TPT bioaccumulates through the food web. However, no such trend was observed for TBT in either area. These results are consistent with data on shallow-water species (Stab et al. 1996).

Results of rearing experiments with marine fish have shown that the BCF of TPT (3500) is less than that of TBT (5000) (Yamada and Takayanagi 1992), whereas the biomagnification factor (BMF) which is calculated as a ratio of concentration in marine fish to that in their feed of TPT (0.57) is greater than that of TBT (0.26–0.38) (Yamada et al. 1994), suggesting that TPT is more likely to bioaccumulate through dietary uptake than TBT. Moreover, the elimination rate constant of TPT (0.020/d) is less than that of TBT (0.035–0.037/d) (Yamada et al. 1994), suggesting that TPT is less easily excreted than TBT and thus remains in organisms. These differences between TBT and TPT can explain the different bioaccumulation patterns of these OTs in the deep-sea ecosystem, i.e., the greater bioaccumulation of TPT through

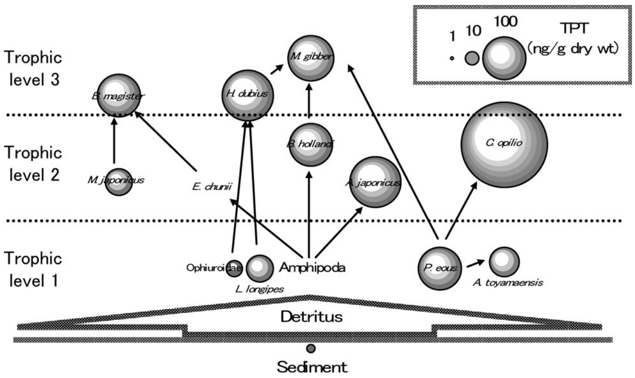

Fig. 6. TPT bioaccumulation through the food web in deep water over the Yamato Bank (B, Fig. 1).

the food web is caused by TPT having a larger BMF and a slower excretion rate than TBT.

Bioaccumulation of TBT and TPT through the benthic food web

Bioaccumulation factors of TPT from sediment to Ophiuroidae, *L. longipes*, *A. toyamaensis*, *E. biunguis*, and *P. eous* which were calculated as a ratio of the average concentration in each organisms to that in sediments over the Yamato Bank were 3.4, 7.6, 9.3, 11, and 19, respectively, and these shrimp accumulated more TPT than Ophiuroidae (Fig. 6). The bioaccumulation factors from sediment to shrimp (7.6–19) were higher than those from shrimp to their predators (*P. eous* to *M. gibber*, 1.1; *L. longipes* to *H. dubius*, 3.5; and *P. eous* to *C. opilio*, 3.7) which were calculated as a ratio of the average concentration in each shrimp to that in their each predators over the Yamato Bank. These results suggest that the transfer of TPT from sediment to shrimp is an important step in the bioaccumulation of TPT through the benthic food web. On the other hand, bioaccumulation factors of TBT from sediment to Ophiuroidae, *L. longipes*, *A. toyamaensis*, *E. biunguis*, and *P. eous* (0.95, 6.4, 0.45, 5.6, and 4.5, respectively), were less than those of TPT. Bioaccumulation factors of TBT from shrimp to their predators (*P. eous* to *M. gibber*, 1.1; *L. longipes* to *H. dubius*, 0.07; and *P. eous* to *C. opilio*, 0.07) were below 1. These results imply that TBT in sediment does not bioaccumulate through the benthic food web.

Laboratory rearing experiment with polychaetes

The concentrations of TBT and TPT in environmentally contaminated marine sediment were 330 and 50 ng/g dry wt, respectively. The concentrations of TBT and TPT in the polychaetes during the 56-d exposure experiment increased substantially from 20 to 73 ng/g dry wt and from 3.9 to 9.8 ng/g dry wt, respectively (Fig. 7); these results demonstrate that polychaetes do accumulate TBT and TPT from the sediment. The ratio of the contaminant concentration in polychaetes to that in sediment for TBT and TPT after 56 d of exposure was

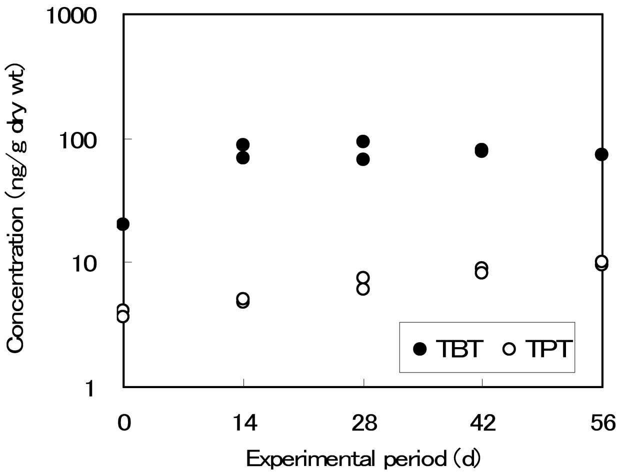

Fig. 7. TBT and TPT concentrations in polychaetes during the exposure experiment.

0.22 and 0.20, respectively. Changes in the TBT concentration from day 14 to day 56 were small, suggesting that TBT concentration had reached equilibrium by day 14. A steady-state concentration of TPT in polychaetes was not achieved during the 56-d exposure period. The result indicates that TPT is less easily excreted by polychaetes than TBT. Thus, the ratio of the steady-state concentration of TPT in polychaetes to its concentration in sediment would be higher than the corresponding TBT ratio.

Conclusions

The finding that TPT concentrations are higher in benthic organisms than in sediments and the results from the laboratory rearing experiment with polychaetes imply that (1) TPT can be transferred to benthic organisms from sediments and then bioaccumulate through the food web and (2) sediments can act as a secondary source of TPT. However, no such trend was observed for TBT. More attention should thus be paid to OTs in sediments as a secondary source, where OTs will remain even if their use in antifouling paints for ships is banned worldwide.

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