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## Trophic Magnification of Triphenyltin in a Marine Food Web of Bohai Bay, North China: Comparison to Tributyltin

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Organotins, especially tributyltin (TBT) and triphenyltin (TPT), are of particular concern due to their ubiquity in the aquatic environment and their toxicity to aquatic organisms. This study reports field studies on trophic magnification factors (TMF) of TBT and TPT in a marine food web. TBT, TPT, and their metabolites in plankton, five benthic invertebrate species, and six fish species collected from Bohai Bay, North China were determined, and it was found that the concentrations of TPT in marine fish were unexpectedly higher than those of TBT. A positive relationship was found between trophic levels and concentrations of TPT, indicating trophic magnification of TPT in this food web. The TMF of TPT was calculated to be 3.70. On the other hand, concentrations of TBT, dibutyltin (DBT) and monobutyltin (MBT) did not exhibit statistically significant trends with trophic levels, and the TMF of TBT was 0.59. Analysis of organotins in the water and surface sediment from Bohai Bay revealed low inputs of TPT to the environment, which indicated that the high concentrations of TPT found in fish from Bohai Bay were due to the food web magnification of TPT.

### Introduction

Organotin pollution in the aquatic environment is of global concern. Two triorganotin compounds, tributyltin (TBT) and triphenyltin (TPT), are toxic to aquatic life (1) and are used worldwide not only as biocides in antifouling paints but also as preserving agents for wood and timber and as fungicides in agricultural activities, resulting in direct release into the water with consequent uptake and accumulation in aquatic fauna (2–4). The worldwide production of organotins in 1996 was approximately 40 000 tons/year (5), and the International Maritime Organization (IMO) has been established to ban the application of organotin antifouling paints on boats after January 1, 2003 and to forbid its usage after 2008. In China, the usage of organotins was estimated to be about 7500 tons/year (6); however, there are still no regulations banning the

application of organotin chemicals including both TBT and TPT. The major source of TBT and TPT in the marine environment comes from their use in antifouling paints. While several studies have demonstrated that TBT is ubiquitous in the aqueous environment, an increasing number of studies have reported the occurrence of TPT in biota (2–4, 7). Some studies have found that the concentrations of TPT are higher than TBT in fish, crab, and mussels from the Japanese Seto Inland Sea (8, 9) and in deep-sea fish from the northwestern Mediterranean Sea (10), although the proportion of TPT used is lower than that of TBT.

One possible cause for the higher concentration of TPT in fish and some other biota is an increase of TPT input into the marine environment compared with that of TBT. In the early 1990s, most developed countries began to restrict TBT-based antifouling coatings for small boats (11), but TPT is used not only as a biocide in antifouling paints but also as a fungicide in agricultural activities for the treatment of potato crops (12). In China, the outputs of TPT used as antifouling paints and as fungicides for the treatment of orchards and cotton plants, which are two potential sources of TPT into aquatic environments, were about 50 and 100 tons/year, respectively (13). The concentrations of TPT and its transformation products, diphenyltin (DPT) and monophenyltin (MPT), have been detected in fresh and marine waters (4, 7, 14–16). The concentration of TPT in marine water and sediment samples is often lower than that of TBT (17–20), but higher TPT concentration (up to 47 ng/L) has been detected in rainwater (21). Alternatively, the higher concentration of TPT than TBT in biota could be attributed to trophic magnification through the food web, because TPT concentrations have been found to be higher in fish than in invertebrates (3, 22), and TPT concentrations in shallow-water fish are lower than those in deep-sea fish (10), which tend to feed at a higher trophic level (TL) than their shallow-water counterparts (23). To our best knowledge, however, there have been no quantitative descriptions of the trophic transfer of organotins in food webs giving the trophic magnification factor (TMF) of TPT (18).

In this study, to clarify the possible causes leading to higher TPT concentrations in biota at high TLs, we used the seawater and surface sediment of Bohai Bay as surrogate measures for TBT and TPT contamination in the bay. We conducted a field study investigating the trophodynamics of organotins in members of a marine food web (including plankton, five benthic invertebrate species, and six fish species) from Bohai Bay in north China, which were proven to be appropriate for testing the trophodynamics of chemicals in our previous papers (24, 25).

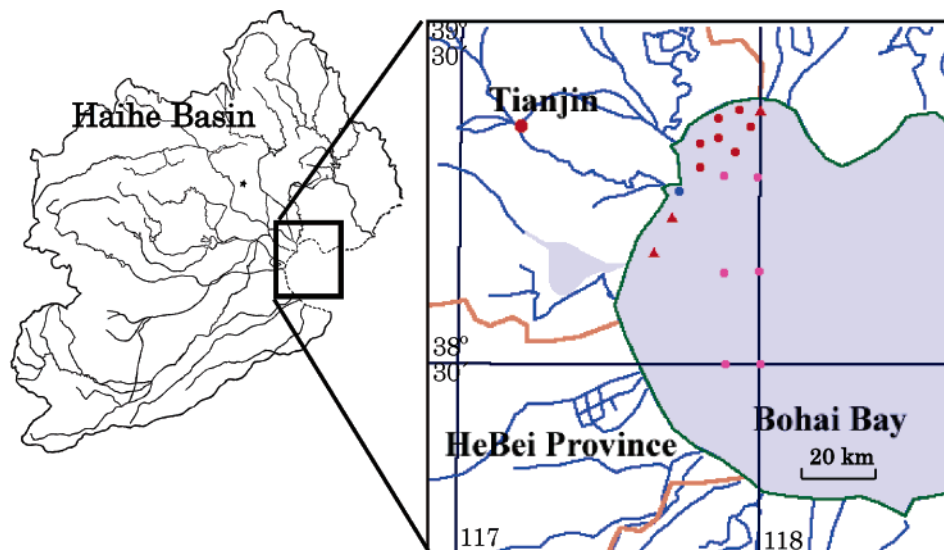
### Materials and Methods

**Chemicals and Standards.** Monobutyltin trichloride (MBT, 97%), monophenyltin trichloride (MPT, 98%), and tropolone (98%) were purchased from ACROS ORGANICS (Geel, Belgium). Diphenyltin dichloride (DPT, 96%) was obtained from Aldrich. Dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 95%), triphenyltin chloride (TPT, 95%), and sodium tetraethylborate (NaBEt<sub>4</sub>, 98%) were purchased from Wako (Osaka, Japan). Deuterated organotins, MBT-*d*<sub>9</sub>, DBT-*d*<sub>18</sub>, TBT-*d*<sub>27</sub>, tetrabutyltin-*d*<sub>36</sub> (TeBT-*d*<sub>36</sub>), MPT-*d*<sub>5</sub>, DPT-*d*<sub>10</sub>, and TPT-*d*<sub>15</sub> were from Hayashi Pure Chemicals (Tokyo, Japan). Dichloromethane, methanol, and hexane were HPLC grade obtained from Fisher Scientific (New Jersey, U.S.A.), and tetrahydrofuran was HPLC grade obtained from DIKMA

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**FIGURE 1.** Location of sampling sites: ● in blue, harbor; ● in pink, sampling locations of planktons; ▲, sampling locations of fish and invertebrates; ● in pink, blue, and red, sampling locations of surface water and sediments.

(U.S.A.). Diethyl ether was HPLC grade and purchased from Siyou Chemicals (Tianjin, China). Acetic acid, hydrochloric acid, and sodium acetate were AR grade. Anhydrous sodium sulfate and sodium chloride were heated at 450 °C for 6 h before usage. Florisil columns (1 g) were obtained from Waters (Massachusetts, U.S.A.). Water was obtained by a compact ultrapure water system (Easypure UV, U.S.A.). Fresh NaBEt<sub>4</sub> solution of 5% (w/v) was prepared with tetrahydrofuran every month. An acetate buffer was made from acetic acid and sodium acetate solution. All the solutions were stored at 4 °C in the dark.

**Samples.** Aquatic food web components were collected in May, June, and September 2002 in the Bohai Bay (Figure 1). These components were the same as those used in our previous papers (24, 25) and were used to describe the trophic transfer of dioxins and nonylphenol. The part of the marine food web investigated in this study included three categories: primary producers (phytoplankton/eston and zooplankton), five invertebrate species (crab (*Portunus trituberculatus*), burrowing shrimp (*Upogebia* sp.), short-necked clam (*Ruditapes philippinarum*), veined rapa whelk (*Rapana venosa*), and bay scallop (*Argopecten irradians*)), and six fish species (weever (*Lateolabrus japonicus*), catfish (*Chaetrichthys stigmatias*), bartail flathead (*Platycephalus indicus*), white flower croaker (*Nibea albiflora*), wolffish (*Obontamblyopus rubicundus*) and mullet (*Liza so-iuy*)). Primary producers were obtained from six locations (39°, 00' N, 117°, 53' E; 39°, 00' N, 118°, 00' E; 38°, 45' N, 117°, 53' E; 38°, 45' N, 118°, 00' E; 38°, 30' N, 117°, 53' E, and 38°, 30' N, 118°, 00' E) by vertical tows (bottom to surface) using 31.6 cm i.d. × 140 m long nets (77 μm mesh) and 37 cm i.d. × 140 m long nets (160 μm mesh), respectively. The phytoplankton/eston samples mainly consisted of algae of the taxonomic groups Bacillariophyta and Pyrrophyta, and the samples of zooplankton mainly consisted of small copepods (*Acartia bifilosa*, *Paracalanus parvus*, *Labidocera euchaeta*, and *Oithona similis*), which are primary herbivores. Invertebrates and fish were both caught with a bottom trawl. Table 2 shows the numbers of samples for each species analyzed.

A sampling map for 14 water and surface sedimentary samples is shown in Figure 1. The surface water samples (0–50 cm beneath the surface) and sediment samples (0–30 cm beneath the surface) were collected in September 2002. The water samples were stored in polycarbonate bottles at 4 °C and analyzed soon after collection. The sediment and biota samples were stored at –20 °C prior to analysis.

**TABLE 1.** Ions Monitored in SIM Mode

chemicals	monitored ions
MBT	149, 179, 233, 235
MBT- <i>d</i> <sub>9</sub>	180, 242, 244
DBT	149, 179, 207, 263
DBT- <i>d</i> <sub>18</sub>	217, 279, 281
TBT	149, 177, 207, 263
TBT- <i>d</i> <sub>27</sub>	153, 190, 217
TeBT- <i>d</i> <sub>36</sub>	190, 254, 318
MPT	195, 253, 255
MPT- <i>d</i> <sub>5</sub>	202, 258, 260
DPT	275, 301, 303
DPT- <i>d</i> <sub>10</sub>	285, 311, 313
TPT	197, 349, 351
TPT- <i>d</i> <sub>15</sub>	202, 364, 366

**Sample Preparation.** Several analytical methods have been developed for the determination of organotin compounds in biota samples. In this experiment, the extraction method was conducted following the methods in previous papers (3, 26), and the cleanup procedure was conducted following the methods reported in a previous paper (27) with some modifications. Frozen biota samples were thawed for 12 h and homogenized using an analytical mill. Then air-dried sediment (5 g) and biota samples (5 g, including wet homogenized phytoplankton/eston and zooplankton, soft tissues of invertebrates, and the muscles of fish) were spiked with deuterium-labeled surrogate analogues (MBT-*d*<sub>9</sub>, DBT-*d*<sub>18</sub>, TBT-*d*<sub>27</sub>, MPT-*d*<sub>5</sub>, DPT-*d*<sub>10</sub>, and TPT-*d*<sub>15</sub>). The spiked samples were extracted with 30 mL of 0.03% (w/v) tropolone in methanol solution together with 2 mL of concentrated hydrochloric acid by ultrasonic shaking for 30 min. Then, the samples were centrifuged for 10 min, and the supernatant was transferred to a separation funnel containing 100 mL of 30% (w/v) NaCl–water solution and 30 mL of dichloromethane. The extraction procedure was repeated three times. After the separation funnel was shaken for 3 min three times, the organic layer was collected and concentrated almost to dryness. The concentrate was mixed with buffer solution (pH = 5.0) and NaBEt<sub>4</sub> to derivatize target organotins. Then, only for biota samples, the derivatized samples were refluxed for about 1 h in 50 mL of 1 N KOH–ethanol solution. After saponification, the ethylated organotins were extracted with about 2 mL of hexane three times. The hexane extract was first concentrated and passed through a florisil cartridge

**TABLE 2. Concentrations (ng/g Wet Weight) of MBT, DBT, TBT, MPT, DPT, and TPT in Organisms Collected from Bohai Bay, North China**

species	tissue lipid %	trophic level <sup>a</sup>	MBT	DBT	TBT	MPT	DPT	TPT	n <sup>b</sup>
phytoplankton/seston	2.4	1.61 ± 0.14	6.9 ± 1.4	19.3 ± 3.9	13.3 ± 2.7	ND	ND	1.4 ± 0.3	3 <sup>c</sup>
zooplankton	1.8	2.00 ± 0.14	11.9 ± 2.4	8.8 ± 1.8	6.0 ± 1.2	ND	ND	1.2 ± 0.2	3 <sup>c</sup>
bay scallop	6.4	2.15 ± 0.12	8.8 ± 1.7	17.1 ± 3.6	24.8 ± 5.2	ND	ND	4.3 ± 0.7	4
crab	6.4	3.1 ± 0.17	3.4 ± 1.5	4.7 ± 0.4	4.7 ± 2.3	ND	2.3 ± 1.1	16.5 ± 6.6	4
burrowing shrimp	7.2	3.16 ± 0.14	14.9 ± 10.6	4.9 ± 0.7	3.1 ± 1.1	ND	ND	17.0 ± 5.3	4
short-necked clam	4.1	2.17 ± 0.2	3.5 ± 0.8	4.9 ± 0.7	3.6 ± 1.4	ND	ND	2.9 ± 0.4	4
veined rapa whelk	6.2	2.79 ± 0.12	3.7 ± 1.1	8.9 ± 0.5	5.0 ± 2.3	ND	ND	4.5 ± 0.4	4
catfish	4.4	3.67 ± 0.04	5.4 ± 0.8	12.4 ± 1.0	1.3 ± 0.3	ND	ND	9.2 ± 0.6	3
weever	4.7	3.88 ± 0.49	4.8 ± 1.5	10.8 ± 0.2	14.6 ± 6.2	ND	ND	11.0 ± 3.6	3
bartail flathead	2.3	3.65 ± 0.24	8.7 ± 2.3	4.8 ± 0.2	2.9 ± 0.6	ND	4.7 ± 1.1	34.7 ± 8.1	4
wolfish	4.0	3.58 ± 0.11	7.7 ± 1.3	6.5 ± 0.6	1.3 ± 0.9	ND	3.7 ± 1.5	30.7 ± 8.4	4
mullet	4.7	3.01 ± 0.44	2.8 ± 0.7	8.1 ± 0.6	3.3 ± 1.1	ND	ND	7.5 ± 5.8	4
white flower croaker	3.1	3.65 ± 0.39	3.0 ± 0.7	2.9 ± 0.2	6.9 ± 1.5	ND	1.4 ± 0.7	26.0 ± 4.8	4

<sup>a</sup> From ref 43. <sup>b</sup> Sample number. <sup>c</sup> Three samples taken from six locations.

column covered with a layer of sodium sulfate and eluted with hexane/diethyl ether (9:1). Finally, the eluant was concentrated to 0.3 mL for biota samples or 0.1 mL for sediment samples, and TeBT-*d*<sub>36</sub> was added prior to gas chromatography mass spectrometric (GC-MS) analysis.

Analysis of organotins in water samples was conducted following a method reported in a previous paper (28). About 20 mL of water was spiked with six deuterated organotins in 40 mL amber glass vials sealed with PTFE-lined silicon septa. After 2 mL of acetate buffer and 0.1 mL of 5% NaBEt<sub>4</sub> solution had been added, the vials were immediately closed and stirred on a magnetic stirrer. Then, the SPME fiber was exposed to the headspace over the vigorously stirred solution at room temperature to analyze TBT, DBT, MBT, and MPT and immersed into the solution to analyze TPT and DPT. After 20 min, the fiber was withdrawn into the needle of the holder and the SPME was placed in the GC injector for analysis.

GC-MS analysis was performed with a Hewlett-Packard 5890 gas chromatograph connected to a Hewlett-Packard 5971 mass spectrometer. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. The injector temperature was maintained at 270 °C, and the detector source temperature was kept at 280 °C. An HP-5MS capillary column (60 m × 0.25 mm i.d. with a film thickness of 0.25 μm) used for organotin analysis was programmed to increase from 60 (2 min) to 130 °C at a rate of 20 °C/min (26 min), and then to 280 °C at 20 °C/min (7 min). The injection volume was 1 μL, and the splitless mode was used. Quantitative analysis was performed using selected ion monitoring mode, and the fragment ions were selected according to the most abundant ions in each oligomer. These ions are listed in Table 1. The concentrations of organotin compounds are expressed as cationic species.

**Quantitation and Quality Assurance Quality Control (QA/QC).** All equipment rinses were done with methanol to avoid sample contamination, and a laboratory blank was incorporated in the analytical procedure. For calibration purposes, a certain amount of six organotin standards and their respective deuterium-labeled organotins in methanol solution was added to 50 mL of acetate buffer solution (pH = 5.0). The standards and their respective deuterium-labeled organotins were derivatized by adding 200 μL of 5% (w/v) NaBEt<sub>4</sub> in tetrahydrofuran as with the samples. Finally, the standard mixture was extracted with 2 mL of hexane three times, and the extracts were combined and concentrated. This procedure was followed daily to prepare fresh standard mixtures by derivatization.

For all sample materials, fortification experiments were performed with the addition of six deuterium-labeled sur-

rogate analogues corresponding to about 5–50 ng/g wet weight for biota samples and 2–10 ng/g for sedimentary samples (equivalent to typical contamination levels). Recoveries of deuterium-labeled surrogates were calculated by response relative to that of the internal standard, TeBT-*d*<sub>36</sub>. The recoveries for sedimentary samples were 63 ± 17% for MBT-*d*<sub>9</sub>, 93 ± 18% for DBT-*d*<sub>18</sub>, 104 ± 22% for TBT-*d*<sub>27</sub>, 77 ± 9% for DPT-*d*<sub>10</sub>, and 63 ± 12% for TPT-*d*<sub>15</sub> (*n* = 5), but the recovery of MPT-*d*<sub>5</sub> was limited to 15% (*n* = 5). For biota samples, while the recoveries were 90 ± 8% for MBT-*d*<sub>9</sub>, 90 ± 7% for DBT-*d*<sub>18</sub>, 103 ± 10% for TBT-*d*<sub>27</sub>, and 83 ± 8% for TPT-*d*<sub>15</sub> (*n* = 6), the recoveries of MPT-*d*<sub>5</sub> and DPT-*d*<sub>10</sub> were limited to 26% and 46% (*n* = 6). In this study, six organotins were quantified in sample extracts relative to their respective deuterium-labeled surrogate analogues. This stable-isotope dilution quantitation method served as an automatic correction for losses of analytes during extraction or sample preparation, as well as for variations in instrument response from injection to injection. Furthermore, the deuterium-labeled surrogates were used as a constant quality control check, as their calculated recoveries from the samples should mimic the recoveries of their unlabeled analyte analogues. The detection limits of MBT, DBT, TBT, MPT, DPT, and TPT at S/N = 3 were 0.4 ± 0.1, 0.2 ± 0.1, 0.2 ± 0.1, 1.0 ± 0.4, 0.2 ± 0.1, and 0.12 ± 0.02 ng/g (dry weight) in sedimentary samples (*n* = 5), 0.7 ± 0.1, 0.6 ± 0.1, 0.8 ± 0.1, 2.5 ± 0.5, 1.0 ± 0.5, and 0.6 ± 0.1 ng/g wet weight in biota samples (*n* = 6), and 1.5 ± 0.2, 2.4 ± 0.2, 4.1 ± 0.4, 3.6 ± 0.4, 5.1 ± 0.5, and 6.8 ± 0.7 ng/L in water samples (*n* = 5).

**Lipid Content.** To determine the lipid content of the analyzed samples, about 5 g of wet samples were ground with anhydrous sodium sulfate, and Soxhlet extraction was carried out for 24 h using 200 mL of dichloromethane/methanol (7:3 v/v) mixture solution. The extracts were then rotated to dry and heated at 65 °C for about 30 min, and lipid amounts were determined gravimetrically.

**Trophic Magnification Factor Calculations.** Studies of contaminant magnification in food webs have used a continuous integrative measure of trophic position based on stable nitrogen isotope ratios (29, 30). The trophic position (TL)

$$TL_{\text{consumer}} = 2 + (\delta^{15}N_{\text{consumer}} - \delta^{15}N_{\text{zooplankton}})/3.8 \quad (1)$$

has been converted using  $\delta^{15}N$  as an index (31). An increasing number of studies have reported trophic transfer of contaminants by correlating the concentration in food web organisms and TL (24, 25, 32–34), and the TMFs are based on the relationships between the TL and the organotin



concentration using simple linear regression:

$$\log \text{organotin concentration} = a + bTL \quad (2)$$

In eq 2,  $b$  was used to calculate TMF by the following equation:

$$TMF = 10^b \quad (3)$$

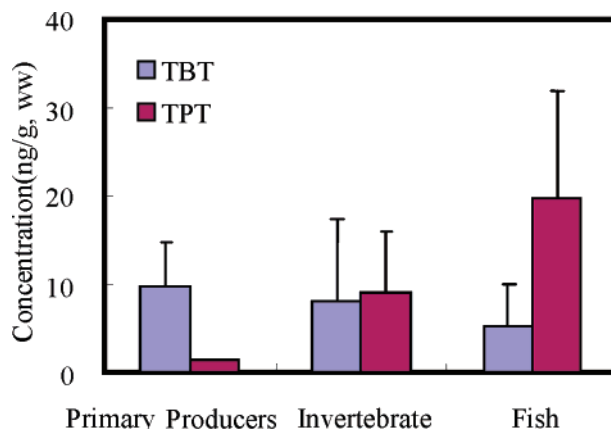
Correlations between concentrations and TLs were examined by Pearson's rank correlation test, and when the value of  $p$  was below 0.05, the linear regression between concentration and TL was regarded as significant.

## Results and Discussion

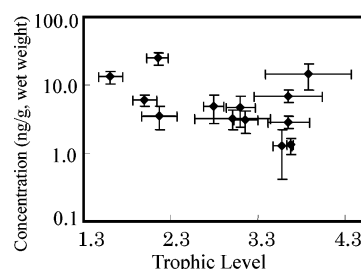
**Organotin Concentrations in Seawater and Sediment.** Seawater and surface sediment samples from 14 sampling sites (Figure 1) of Bohai Bay were used as surrogate measures for TBT and TPT contamination in the bay. While the mean TBT concentration in seawater was  $9.8 \pm 8.7$  ng/L ( $n = 20$ ) (35), the TPT concentrations were below the detection limit (6.8 ng/L). Concentrations of both TBT and TPT were significantly lower than those in western Mediterranean coastal enclosures (7) and in Otsuchi Bay, Japan (19). The mean concentration of TBT in surface sediment was 0.7 ng/g dry weight, and the concentrations ranged from no detection to 2.3 ng/g, except for the sample taken from the port, which had a TBT concentration of 40.6 ng/g dry weight. The TBT concentrations in sedimentary samples were lower than those in sediment from Otsuchi Bay (19, 36) and Osaka Bay, Japan (37) and in the coastal marine environment of Indonesia (38). TPT was detected in only four samples among the 14 sampling sites (near the detection limit of 0.1 ng/g dry weight), and the concentrations were also lower than that from Otsuchi Bay, Japan (19).

**Organotin Concentrations in Marine Biota from Bohai Bay.** The organotin compounds analyzed in this study included MBT, DBT, DBT, MPT, DPT, and TPT, and the results are provided in Table 2. Three butyltins (MBT, DBT, and TBT) were detected in samples from all species of biota studied. The concentrations of TBT in fish samples were slightly higher than those from other Asian and Oceanian countries such as India, Bangladesh, Thailand, Vietnam, and Indonesia (39). And the concentrations of TBT in clams and scallops were significantly lower than those from Hong Kong and Malaysia but were similar to those from Indonesia (40). Of the three phenyltins, only TPT was detected in all biota. DPT was detected only in crab, bartail flathead, wolffish, and white flower croaker, and no MPT was detected in any biota. This profile of organotins in the biota from Bohai Bay is similar to that of biota from a shallow freshwater lake in The Netherlands (3) and in marine biota from the German Environmental Specimen Bank (41). Figure 2 shows a comparison of the mean concentrations of TPT and TBT in primary producers (phytoplankton/seston and zooplankton), five invertebrate species (crab, burrowing shrimp, short-necked clam, veined rapa whelk, and bay scallop), and six fish species (weever, catfish, bartail flathead, white flower croaker, wolffish, and mullet) taken from Bohai Bay in north China. It was found that the mean concentration of TPT ( $19.9 \pm 12.0$  ng/g wet weight) in fish ( $n = 22$ ) was significantly higher than that of TBT ( $5.1 \pm 5.1$  ng/g wet weight); however, in primary producers, the mean concentration of TPT was lower than that of TBT, and in invertebrate species TPT concentration was similar to TBT. These results are similar to that observed in a freshwater food web (3).

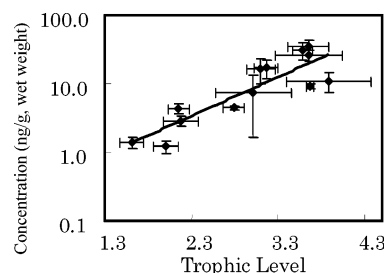
**Trophic Transfer of Organotins.** It has been reported that the animal  $\delta^{13}C$  is largely determined by its diet (42). The  $\delta^{13}C$  values for fish ( $-18.57$  to  $-12.30$ ) were similar to those for invertebrates ( $-18.87$  to  $-14.63$ ) as reported in our previous paper (43). In our previous research, the TL of the



**FIGURE 2.** Comparison of TBT and TPT concentrations in primary producers, invertebrates, and fish collected from Bohai Bay. The error bars of the primary producers, invertebrates, and fish correspond with the standard deviations of organotin concentrations in the primary producers including phytoplankton/seston and zooplankton; invertebrates including crab (4 specimens), burrowing shrimp (4), short-necked clam (4), veined rapa whelk (4), and bay scallop (4); and fish including catfish (3), weever (3), bartail flathead (4), wolffish (4), mullet (4), and white flower croaker (4), respectively.



**FIGURE 3.** Concentrations of TBT—TL relationships for the marine food web from Bohai Bay.



**FIGURE 4.** Concentrations of TPT—TL relationships for the marine food web from Bohai Bay. The lines represent linear regression.  $p < 0.001$ ,  $r^2 = 0.78$ .

Bohai Bay food web was elucidated using nitrogen stable isotopes (43). In the present study, the TL, as defined by  $\delta^{15}N$ , was used to calculate the TMF of organotins throughout the food web of Bohai Bay. Figure 3 shows the relationships between TLs and the MBT, DBT, and TBT concentrations in biota. Concentrations of TBT in biota appear to decrease slightly with increasing TL in the food web. The decrease of concentrations of TBT with increasing TL did not appear to be statistically significant ( $p = 0.119$ , Figure 3). The TMF of TBT was estimated to be 0.59. Linear regression analysis was also carried out to determine the relationships between the TL and the concentrations of MBT and DBT, and it was found that the concentrations of MBT and DBT in biota did not significantly decrease with TLs ( $p = 0.537$  for MBT and  $p = 0.116$  for DBT). It is interesting that concentrations of TPT in biota significantly increased with their TLs (Figure 4), indicating the trophic magnification of this contaminant

through the food web. The least-squares regression equation of the logarithm of TPT concentration versus TL is as follows:

$$\log[\text{TPT}] = 0.57\text{TL} - 0.77 \quad r^2 = 0.78, \quad p < 0.001 \quad (4)$$

The TMF for TPT was calculated to be 3.70, which was similar to the TMFs for DDE (3.26) and HCB (2.96) in the same food web (24, 25), suggesting that TPT was biomagnified to the same extent as these persistent organochlorines. Because the concentrations of MPT and DPT were not detected in all biota samples, their TMFs could not be obtained in this study.

Taken together, the trophic transfers of TPT and TBT in the food web and contaminant concentrations in water and sediments indicate that the difference of food web magnification between TPT and TBT led to higher TPT concentration in marine biota with higher TLs compared with those of TBT. Although the detailed mechanism causing the different trophodynamic behavior of TBT and TPT is not yet fully understood, the trophic magnification for concentration was proposed to be dependent on hydrophobic partitioning and metabolic transformation. Considering the hydrophobic partitioning, this dependence is difficult to explain because both TBT<sup>+</sup> and TBTOH are more hydrophobic than TPT<sup>+</sup> and TPTOH (44). The reason for trophic magnification of TPT may be the fact that TPT is more difficult to metabolize than TBT. It has been reported that while there is significant metabolism of TBT, no metabolism of TPT was found in *Chironomus riparius* (45). This corresponds well with the results that concentrations of biodegradation products of TBT in the livers of fish were found to be high compared with that of TPT (3).

Some countries such as Canada, the United States, Japan, and Australia are evaluating the persistent, bioaccumulative, and toxic (PBT) potential for existing chemicals, and detailed information on bioaccumulation has become necessary. Bioaccumulation of a chemical is often estimated based on the octanol–water partition coefficient ( $K_{ow}$ ), and a chemical is considered to be bioaccumulative if its log  $K_{ow}$  is more than 5 under the definition of UNEP Long-Range Atmospheric Pollutants (LRTAP). However, with a log  $K_{ow}$  of 3.5 for a neutral species (44), the TPT appears to be biomagnified in the marine aquatic food web, suggesting more reliable alternative methods for predicting bioaccumulation must be developed to fill the gap between prediction and observation.

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