Bull Environ Contam Toxicol (2009) 83:239–243
DOI 10.1007/s00128-009-9752-2

# Butyl and Phenyl Tin Compounds in Fish and Shellfish on the Korean Market

**Chang-Hwan Oh**

Received: 19 October 2008 / Accepted: 24 April 2009 / Published online: 8 May 2009


**Abstract** The degree of organotin contamination was determined in samples of ten species of fish and shellfish that were representative of the Korean fish market. Shellfish and fish samples were collected in the fish markets of eight big cities in Korea (Gangneung, Ulsan, Pusan, Daegu, Guangju, Daejun, Incheon and Seoul). The edible portion of total 160 samples were analyzed for organotin compounds such as monobutltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPT), diphenyltin (DPT) and TPT (triphenyltin) by GC-MSD SIM mode after propylation and Florisil clean-up. Generally organotin levels of fish were higher than shellfish. The highest concentration of TBT was found in mackerel (average 67.02 ng/g-wet wt.) among fish and shellfish. TBT usually accounted higher percentage than that of MBT and DBT in most samples. However, the average concentration order of PTs in the tested samples was MPT > TPT > DPT except saury.

**Keywords** Butyltin · Phenyltin · Fish · Shellfish · Mackerel · Korean market · GC-MSD

The International Convention on the Control of Harmful Anti-fouling Systems on Ships, which came into effect at 17 September 2008, prohibit the use of harmful organotins in anti-fouling paints used on ships (IMO 2006). However, it is possible that even though many countries may sign up to the proposed Anti-fouling Systems, non-signatory nations in the developing world (including the far east) may continue to develop, produce and use tributyl tin (TBT) for some years to come (Kwok and Leung 2005). One of the most effective anti-fouling paints, developed in the 1960s, contains the organotin TBT, which has been proven to cause deformations in oysters and sex changes in whelks (IMO 2006). Organotin compounds have a broad range of applications, including uses such as PVC stabilizers, plastic additives, industrial catalysts, insecticides, fungicides, bactericides, wood preservatives and antifouling paints since the 1960s (Kannan and Tanabe 2009; Stewart and Thompson 1994; Ainsworth 1992). Concern over the ecotoxicological impacts of TBT led to its restriction in most developed countries since the late 1980s. A reduction in TBT contamination was recorded in developed countries after the restriction (Stewart 1996). Chronic toxic effects of TBT such as shell calcification anomalies in oysters and 'imposex' phenomenon in gastropods occur at a few ng TBT/L levels (Gibbs and Bryan 1986; Alzieu 1991; Gibbs and Bryan 1996). It has been documented that TBT disrupts the endocrine system in some mollusks (Matthiessen and Gibbs 1998). In Korea, the government has implemented partial restrictions that prohibit the usage of antifouling paints including trialkyltin hydroxide and its mixtures for coast-wide vessels and aquaculture nets, since March, 2000. The considerable contamination by TBT was reported in mollusks such as oyster and mussel from the coastal water and Chinhae Bay, Korea (Hong et al. 2002; Shim et al. 2000; Hwang et al. 1999). And the assessment results of the TBT (7–797 ng/g) and TPT (8–1,560 ng/g) in starfish and bivalves were reported recently (Shim et al. 2005). However, the contamination status of organotin compounds for the fish and shellfishes around the market of Korea are not reported so far. More information is needed for the contamination of

C.-H. Oh (✉)
Department of Oriental Medical Food and Nutrition, Semyung University, 117 Semyung-ro, Jecheon, Chungbuk 390-711, Korea
e-mail: och35@semyung.ac.kr; changhwan@hanmail.net

seafood materials with butyltin and phenyltin compounds to evaluate the accurate exposure status to the people in Korea. Therefore, the monitoring of the butyl- and phenyltin compounds was performed for total ten species of fish and shellfish products circulated in eight local markets in Korea.

## Materials and Methods

Total one hundred sixty samples consisted with each five kinds of fish and shellfish (Table 1) were purchased from the eight largest local fishery markets located in Gangneung, Ulsan, Busan, Daegu, Gwangju, Daejeon, Incheon and Seoul, South Korea. Each three fish and 1 kg of shellfish was collected as a sample in each sampling site twice during the year 2001 (August and October). All samples were frozen with dry ice right after purchasing in the market along the way to the laboratory followed by storing in deep freezer (−40°C) before analysis. Monobutyltin (MBT) chloride, monophenyltin (MPhT) chloride and diphenyltin (DPhT) chloride were purchased from Aldrich (Milwaukee, WI, USA). Dibutyltin (DBT) chloride and TBT chloride were obtained from Wako Pure Chemicals (Osaka, Japan). Triphenyltin (TPhT) chloride was purchased from Fluka Chemie AF (Buchs, Switzerland). The surrogate standard tripentyltin chloride and internal standard tetrapentyltin chloride were obtained from ABS (Basel, Switzerland) and Aldrich (Milwaukee, WI, USA), respectively. Each organotin standard was dissolved in hexane as a stock solution (1,000 μg/mL). The florisil cartridge column (1 g, 50–200 μm) was obtained from Waters Associates, Inc. (Milford, Massachusetts, USA). The Grignard reagent, propylmagnesium chloride (about 2.0 M in diethyl ether) was purchased from Fluka (Buchs, Switzerland). A metal chelator, tropolone (2-hydroxycyclohepta-2,4,6-trienone) was obtained from Tokyo Chemical Industry Co., LTD. (Tokyo, Japan). The HPLC grade dichloromethane was purchased from Burdick & Jackson (Muskegon, MI, USA). Other reagents and solvents were purchased from Wako Pure Chemicals (Osaka, Japan).

The edible portion of the sample, already measured, were pooled and homogenized in a glass amber bottle. Tripentyltin chloride (2 μg) was added to the samples as a surrogate standard. The samples were digested with 10 mL of 50% (v/v) HCl for 30 min and then extracted with 20 mL dichloromethane with tropolone (0.1%) by shaking for 3 h. After 10 min centrifugation (4,000 rpm), 2 mL of organic phase was transferred to 15-mL glass test tubes and concentrated under a gentle stream of nitrogen. The extracts were dissolved in *n*-hexane (2 mL) and propylated with 200 μl of 2M propylmagnesium chloride for 20 min. The remaining propyl magnesium chloride was neutralized with 4 mL of 0.4N sulfuric acid. The propylated extracts were recovered by centrifugation and cleaned up on florisil cartridge column. The cleaned extracts were concentrated to 1 mL and spiked with tetrapentyltin (2 μg) as an internal standard, and then analyzed by gas chromatograph with mass selective detector (GC-MSD).

For the GC-MSD analysis, Agilent 5973N mass selective detector (MSD) equipped with DB-5MS (30 m × 0.25 mm I.D., 0.25 μm; Agilent J&W Scientific, Folsom, CA, USA) was used with mobile phase helium 1 mL/min constant flow mode. The oven temperature was held constant at 80°C for 2 min, increasing to 280°C with 10°C/min and kept for 45 min. Each 1 μL of sample was injected with split less mode (at 240°C) with purge delay time 8 min. All samples were injected by auto-sampler. The selective ion monitoring (SIM) mode analysis with electron impact mode (70 eV) was performed with target and qualifier ions for each organotin compound (Table 2). The limit of quantification (LOQ) of MBT, DBT, TBT, MPT, DPT and TPT were 0.51, 0.05, 0.03, 0.09, 0.06 and 0.02 ng/g, respectively. To estimate the precision of the analysis method, each seven replicate analyzes were performed for 10 g of granular ark and Japanese flying squid, respectively. The precision was represented as percent relative standard deviation (%RSD) ranged 4.3% (DBT,

**Table 1** Tested fish and shellfish collected in Korean markets

| | Korean name | English name | Academic name |
|---|---|---|---|
| Shellfish | Sora | Spiny top shell | *Batillus cornutus* |
| | Honghab | Hard shelled mussel | *Mytilus edulis* |
| | Ggomak | Granular ark | *Tegillarca granosa* |
| | Bajirak | Japanese carpet shell | *Ruditapes philippinarum* |
| | Gamakjogae | Artemis orientalis | *Cyclina sinensis* |
| Fish | Daegu | Pacific cod | *Gadus macrocephalus* |
| | Godeunger | Mackerel | *Scomber japonicus* houttuyn |
| | Ojinger | Japanese flying squid | *Todarodes pacificus* steenstup |
| | Ggongchi | Saury | *Cololabis saira* |
| | Galchi | Hairtail | *Trichiurus lepturus* linnaeus |

**Table 2** Selective ion monitoring mode conditions for GC-MSD analysis of organotin compounds

| No. | Target compound (abbreviation) | Target ion | Qualifier ion | Qualifier ion ratio% | LOQ | |
|---|---|---|---|---|---|---|
| | | | | | ng/g | RSD% |
| 1 | Monobutyltin (MBT) | 277 | 275 | 275 | 0.51 | 7.5 |
| 2 | Dibutyltin (DBT) | 277 | 275 | 275 | 0.05 | 4.3 |
| 3 | Tributyltin (TBT) | 263 | 261 | 261 | 0.03 | 6.8 |
| 4 | Monopenyltin (MPT) | 351 | 349 | 349 | 0.09 | 5.7 |
| 5 | Diphenytin (DPT) | 317 | 315 | 315 | 0.06 | 4.3 |
| 6 | Tripentyltin[a] | 305 | 303 | 303 | – | – |
| 7 | Triphenyltin (TPT) | 283 | 281 | 281 | 0.02 | 5.6 |
| 8 | Tetrapentyltin[b] | 333 | 331 | 331 | – | – |

[a] Surrogate standard

[b] Internal standard

DPT)–7.5% (MBT). When 20 μg of each organotin were spiked to 10 g of granular ark and Japanese flying squid, the recovery rates ranged 84% (MBT in Japanese flying squid)–97% (TBT in Japanese flying squid).

## Results and Discussion

The widespread occurrence of organotin compounds were detected in fish and shellfish of Korean market. The average concentrations of the butyltins (BTs) in shellfish ranged from 7.23 to 47.62 ng/g for MBT, 8.81 to 18.23 ng/g for DBT, and 11.45 to 23.00 ng/g for TBT. And the average concentrations of the phenyltins (PTs) in shellfish ranged from 3.43 to 7.33 ng/g for MPT, 0.34 to 2.35 ng/g for DPT, and 0.49 to 3.68 ng/g for TPT (Table 3). The total average concentration of ΣBTs was 49.22 ng/g that was much higher than the ΣPTs' (7.59 ng/g). The highest average concentration of ΣBTs (88.85 ng/g wet weight) was found in the Hard shelled mussel, while the lowest average concentration of ΣBTs (27.49 ng/g wet weight) was detected in spiny top shell among the shellfish. MBT, the breakdown product of DBT and TBT accounted highest percentage (54%) of BTs in the hard shelled mussel (Fig. 1). On the other hand, TBT usually accounted higher percentage than that of MBT in the other tested shellfish. Hwang et al. (1999) reported that TBT concentrations in shellfishes collected from eight stations of Chinhae Bay in 1994 ranged from 50 to 500 ng Sn/g (≈24–244 ng TBT/g wet weight) and 40–740 ng Sn/g dry weight (≈49–879 ng TBT/g wet weight). However, the MBT concentration ratio of ΣBTs detected in starfishes *Asterias pectinifera* (86.3%) and *A. amurensis* (57.2%) accounted highest percentage (Shim et al. 2005) which is the similar butyltin composition in the hard shelled mussel of the present study.

**Table 3** Average concentrations (ng/g wet weight) of organotins detected in edible portion of shellfish

| Shellfish | MBT | DBT | TBT | ΣBTs | MPT | DPT | TPT | ΣPTs |
|---|---|---|---|---|---|---|---|---|
| Spiny top shell | 7.23 | 8.81 | 11.45 | 27.49 | 7.33 | 0.71 | 3.68 | 11.72 |
| Hard shelled mussel | 47.62 | 18.23 | 23.00 | 88.85 | 5.99 | 0.69 | 1.56 | 8.25 |
| Granular ark | 11.19 | 15.06 | 18.57 | 44.82 | 3.43 | 0.34 | 0.49 | 4.26 |
| Japanese carpet shell | 16.16 | 11.62 | 18.17 | 45.95 | 3.96 | 1.26 | 0.80 | 6.02 |
| Artemis orientalis | 11.76 | 11.30 | 15.92 | 38.97 | 2.95 | 2.35 | 2.39 | 7.70 |
| Average | 18.79 | 13.00 | 17.42 | 49.22 | 4.74 | 1.07 | 1.78 | 7.59 |

The average concentration of ΣPTs was much lower than that of ΣBTs that is similar to that of marine fishery products on the Japanese market (Ueno et al. 1999). The highest average concentration of ΣPTs (11.72 ng/g wet weight) was found in the spiny top shell, while the lowest average concentration of ΣPTs (4.26 ng/g wet weight) was detected in granular ark among the shellfish.

The average concentration order of PTs in tested shellfish was MPT > TPT > DPT. The highest MPT ratio was observed on granular ark (81%) followed by hard shelled mussel (73%), Japanese carpet shell (66%), spinytop shell (63%) and artemis orientalis (38%).

The average concentrations of ΣBTs (51.27 ng/g) and ΣPTs (7.59 ng/g) in fish were higher than those of shellfish. Not like the result of shellfish, the average concentrations of TBT were higher than MBT in each fish (except Pacific cod) that is same to the result of Ueno et al. (Ueno et al. 1999). The average concentrations of the butyltins (BTs) in fish ranged from 8.54 to 35.61 ng/g for MBT, 9.38 to 16.88 ng/g for DBT, and 11.92 to 67.02 ng/g for TBT. And the average concentrations of the phenyltins (PTs) in fish ranged from 0.23 to 31.39 ng/g for MPT, 0.05 to 1.49 ng/g for DPT, and 0.04 to 7.73 ng/g for TPT (Table 4).

Interestingly, the highest concentrations of BTs and PTs were recorded in mackerel. Especially more than 50 ng/g of TBT concentrations (83.60, 110.76, 123.17, 139.73 and 379.16 ng/g) were all detected in mackerel collected in Daegu, Gwangju, Incheon, Daejeon and Seoul. No other tested fishes showed more than 24 ng/g of TBT (saury collected in Seoul) except mackerel. According to

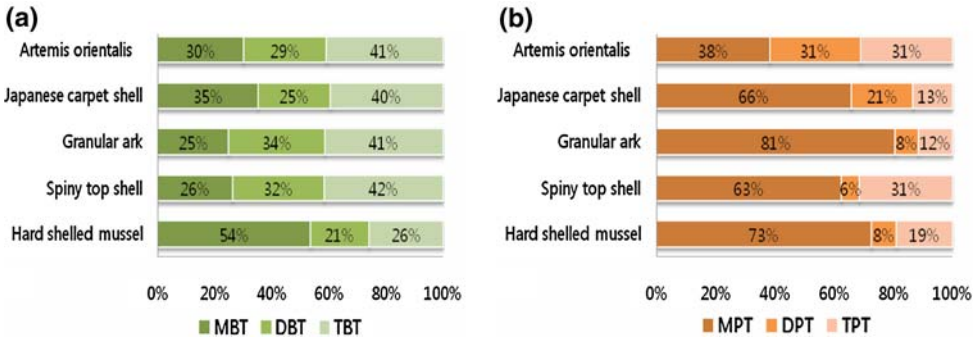


**Fig. 1** Spatial normalized distribution of (**a**) butyltin and (**b**) phenyltin average concentration ratios in shellfish collected in fish markets, Korea

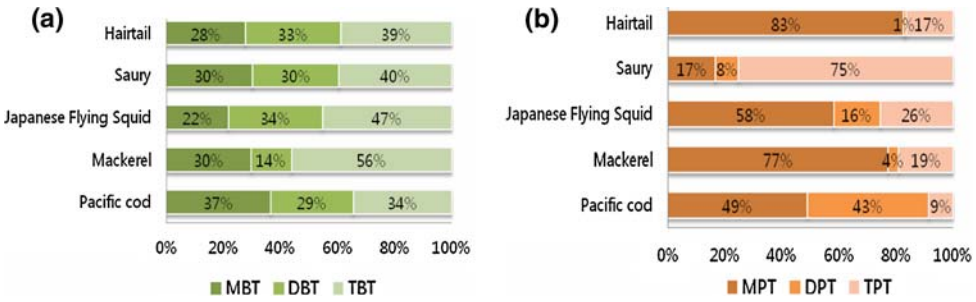


**Fig. 2** Spatial normalized distribution of (**a**) butyltin and (**b**) phenyltin average concentration ratios in fish collected in fish markets, Korea

**Table 4** Average concentrations (ng/g wet weight) of organotins detected in each edible portion of fish

| Fish | MBT | DBT | TBT | ΣBTs | MPT | DPT | TPT | ΣPTs |
|---|---|---|---|---|---|---|---|---|
| Pacific cod | 15.25 | 12.09 | 14.36 | 41.70 | 0.23 | 0.20 | 0.04 | 0.47 |
| Mackerel | 35.61 | 16.88 | 67.02 | 119.51 | 31.39 | 1.49 | 7.73 | 40.61 |
| Japanese flying squid | 7.49 | 11.38 | 15.54 | 33.40 | 3.44 | 0.96 | 1.51 | 5.91 |
| Saury | 9.36 | 9.38 | 12.28 | 31.01 | 0.76 | 0.37 | 3.41 | 4.54 |
| Hairtail | 8.54 | 10.25 | 11.92 | 30.71 | 5.16 | 0.05 | 1.03 | 6.24 |
| Average | 15.25 | 11.99 | 24.02 | 51.27 | 8.19 | 0.62 | 2.74 | 11.55 |

Sudaryanto et al. (2004), mackerel and long-jawed mackerel also represented relatively high concentration of ΣBTs (mackerel: 80 ng/g wet wt. from Ktabahru and long-jawed mackerel: 78 ng/g wet wt. from Mersing). The high accumulation of BTs in the above two fishes was explained as the particular ecological behavior of that they are found throughout the offshore region and have long distance migration behavior. During migration, probably, they may integrate contaminants from a wide range of geographic area of the busy shipping traffic line (Sudaryanto et al. 2004). And the relatively higher TBT/ΣBTs ratio (56%) and the high accumulated ΣBTs in mackerel could be conjectured as it may have a particular metabolic system comparing to other fishes. Concerning the PTs, the ΣPTs of mackerel (40.61 ng/g) was almost 86 times larger than that of pacific cod (0.47 ng/g) which is the fish possessing the lowest amount of ΣPTs among the tested fish. In contrast with the relatively high TBT ratio among BTs in fish, the breakdown product MPT ratio was dominant among PTs in fish except saury in which almost 75% of PTs was composed with TPT. The highest MBT ratio was observed on hairtail (83%) followed by mackerel (77%), Japanese flying squid (58%) and pacific cod (49%) (Fig. 2).

Relatively significant positive relationships ($R = 0.4$) were observed between ΣBTs and ΣPTs concentrations in the artemis orientalis and spiny top shell. However, the other shellfish and fish showed very low or almost no correlation between ΣBTs and ΣPTs concentrations.

The present work showed that the characteristic residual composition of the organotin compounds in the frequently consumed shellfish and fish in Korea. Further study might be needed to reveal the reason for the comparatively high concentration of organotin compounds found in mackerel with considering the highest intake amount of mackerel among fish and shellfish (except the processed fish cake) in Korea.

**Acknowledgments** This study was supported by Korea Food & Drug Administration, Korea. The author thanks H. K. Choi and H. Song for supporting sampling and sample preparation for the analysis.

## References

Ainsworth SJ (1992) Plastic additives. Chem Eng News 31:169–179

Alzieu C (1991) Environmental problems caused by TBT in France: assessment, regulations, prospects. Mar Environ Res 32:7–17. doi:10.1016/0141-1136(91)90029-8

Gibbs PE, Bryan GW (1986) Reproductive failure in populations of the dog-whelk, *Nucella lapillus*, caused by imposex induced by

tributyltin from antifouling paints. J Mar Biol Assoc UK 66:767–777

Gibbs PE, Bryan GW (1996) TBT-induced imposex in neogastropods snail: masculinization to mass extinction. In: de Mora SJ (ed) Case Study of an Environmental Contaminat. Cambridge University Press, Cambridge, p 212–236

Hong HK, Takahashi S, Min BY, Tanabe S (2002) Butyltin residues in blue mussels (*Mytilus edulis*) and arkshells (Scapharca broughtonii) collected from Korea coastal waters. Environ Pollut 117:475–486. doi:10.1016/S0269-7491(01)00185-3

Hwang HM, Oh JR, Kahng SH, Lee KW (1999) Tributyltin compounds in mussels, oysters and sediments of Chinhae Bay, Korea. Mar Environ Res 47:61–70. doi:10.1016/S0141-1136(98)00023-3

IMO (2006) International convention on the control of harmful antifouling systems on ships, Available from: http://www.imo.org/conventions/mainframe.asp?topic_id=529. Accessed Mar 07, 2009

Kannan K, Tanabe S (2009) Global contamination by organotin compounds. In: Arai T, Harino H, Ohji M, Langston WJ (eds) Ecotoxicology of antifouling biocides. Part II. Springer, Tokyo, p 39–60

Kwok KWH, Leung KMY (2005) Toxicity of antifouling biocides to the intertidal harpacticoid copepod Tifriopus japonicus (Crudtacea, Copepoda): effects of temperature and salinity. Mar Pollut Bull 51:830–837. doi:10.1016/j.marpolbul.2005.02.036

Matthiessen P, Gibbs PE (1998) Critical appraisal of the evidence for tributyltin-mediated endocrine disruption in mollusks. Environ Toxicol Chem 17:37–43. doi:10.1897/1551-5028(1998)017<0037:CAOTEF>2.3.CO;2

Shim WJ, Kahng SH, Hong SH, Kim NS, Kim SK, Shim JH (2000) Imposex in the rock shell, Thais clavigera, as evidence of organotin contamination in the marine environment of Korea. Mar Environ Res 49:435–451. doi:10.1016/S0141-1136(99)00084-7

Shim WJ, Yim UH, Kim NS, Hong SH, Oh JR, Jeon JK, Okamura H (2005) Accumulation of butyl- and phenyltin compounds in starfish and bivalves from the coastal environment of Korea. Environ Pollut 133:489–499. doi:10.1016/j.envpol.2004.06.018

Stewart C (1996) The efficacy of legislation in controlling tributyltin in the marine environment. In: de Mora SJ (ed) Case study of an environmental contaminant. Cambridge University Press, Cambridge, p 264–297

Stewart C, Thompson JAJ (1994) Extensive butyltin contamination in Southwestern coastal British Columbia, Canada. Mar Pollut Bull 28:601–606. doi:10.1016/0025-326X(94)90361-1

Sudaryanto A, Takahashi S, Iwata H, Tanabe S, Ismail A (2004) Contamination of butyltin compounds in Malaysian marine environments. Environ Pollut 130:347–358. doi:10.1016/j.envpol.2004.01.002

Ueno S, Susa N, Furukawa Y, Komatsu Y, Koyama S, Suzuki T (1999) Butyltin and phenyltin compounds in some marine fishery products on the Japanese market. Arch Environ Health 54:20–25