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Baseline

Accumulation of butyltin compounds in cetaceans from Korean coastal waters

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ABSTRACT

Data on the occurrence and accumulation profiles of butyltins (BTs), including tributyltin (TBT), in marine mammals are scarce. This is the first study to investigate residue levels and accumulation patterns of BTs in cetaceans from Korean coastal waters. The total concentrations of BTs (sum of mono- to tri-butyltins) in minke whales (*Balaenoptera acutorostrata*) and long-beaked common dolphins (*Delphinus capensis*) ranged from 15.7 to 297 ng/g wet weight (mean: 100 ng/g wet weight) and from 59.0 to 412 ng/g wet weight (mean: 228 ng/g wet weight), respectively. Dibutyltin (DBT) accounted for 63% of the total BTs in all cetacean samples. Significant species-specific differences in BT concentrations, possibly due to the differences in their habitat and diet, were found between the two cetacean species. The concentrations of DBT and TBT in most cetacean samples exceeded the threshold value for cytotoxic effects in cetaceans, implying potentially adverse health risks from exposure to BTs.

Butyltins (BTs) are of great concern in aquatic ecosystems because of their toxicity and ecotoxicological risk. BTs such as tributyltin (TBT) had been widely used as an antifouling paint component on ship hulls, marine platforms and fishing nets, resulting in worldwide aquatic pollution. Many studies have reported the adverse effects of TBT on non-target marine organisms; for example, high mortality in mussels (Beaumont and Budd, 1984), imposex in neogastropods (Ellis and Pattisina, 1990; Leung et al., 2006), shell deformations of oysters (Axiak et al., 1995), and sterilization in gastropods (Oehlmann et al., 1996). Adverse biological effects and contamination from BTs resulted in the restriction of use of TBT in antifouling paints. As a consequence, environmental concentrations of BTs have been decreasing (Sousa et al., 2007; Rato et al., 2009); however, BTs are still detected in aquatic ecosystems and high BT concentrations have been found in estuaries and harbors (Leung et al., 2006; Berto et al., 2007). In Korea, nationwide contamination from BTs is comparable to, or lower than in developed countries (Choi et al., 2009a); however, high TBT concentrations are reported near shipyards and industrialized harbors in Ulsan, Busan, and Okpo with the biggest shipbuilding industrial activities in the world (Shim et al., 2002; Choi et al., 2009b).

Marine mammals have long life-spans and occupy a high trophic status in food chains, and accumulate high levels of BTs (Kannan et al., 1997; Nakata et al., 2002; Murata et al., 2008; Nakayama et al., 2009). BTs contamination in marine mammals may cause immunosuppressive effects leading to infectious diseases or opportunistic infection by pathogens (Kannan et al., 1998; Strand et al., 2005). Nakata et al. (2002) suggested the possibility that BTs could pose a serious threat to the immune functions in free-ranging marine mammals and in humans. Nakayama et al. (2009) also reported that BTs could be a factor affecting parasitic infection in finless porpoises.

Although there are reports on BTs in marine mammals worldwide, no data are available on BTs in marine mammals from Korean coastal waters. In Korea, many cetaceans are taken as by-catch in fishing nets, although a ban on commercial whaling was implemented in 1986. In 2006, a total of 587 cetaceans were reported to be caught through by-catch in Korean coastal waters (An and Kim, 2008). Minke whales (*Balaenoptera acutorostrata*; Family *Mysticeti*) and long-beaked common dolphins (*Delphinus capensis*; Family *Odontoceti*) collectively accounted for 75% of the by-catch of cetaceans. The objective of the present study is to investigate contamination status, accumulation patterns and ecotoxicological effects of BTs in minke whales, and long-beaked common dolphins from Korean coastal waters.

Liver samples were obtained from minke whales and long-beaked common dolphins entangled in fishing nets along the Korean coast in 2006. The minke whales were caught off the whole Korean coast while the common dolphins were caught off the east coast. The minke whales were caught throughout the year and common dolphins were caught in the spring months. Body length of the cetaceans was determined in the field and sex was determined genetically from skin samples. After biometric measure-

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ments, the cetaceans were dissected and transported to the Cetacean Research Institute laboratory, located in Ulsan, Korea. All the samples were stored at −20 °C until extraction.

Detailed procedures for analysis of BTs in biota are described elsewhere (Choi et al., 2009a, 2010). In brief, approximately 3 g samples were extracted twice by mechanical shaking with 0.1% tropolone (Merck, Hohenbrunn, Germany)-methylene chloride (Merck, Darmstadt, Germany), and 50% HCl (Merck, Darmstadt)-methanol (Merck, Darmstadt) in 50-ml Teflon tubes. Tripentyltin chloride (Kanto, Tokyo, Japan) was spiked, as a surrogate standard, before extraction. The extract was hexylated with a Grignard reagent, N-hexylmagnesium bromide (Tokyo Chemical Industry, Tokyo). The remaining Grignard reagent was removed with 1 N H_2SO_4 (Merck, Hohenbrunn). The organic fraction was decanted, concentrated with a Turbo vap LV (Caliper Life Science Inc., Hopkinton, MA, USA), and then cleaned by passage through a florisil (60–100 mesh, reagent grade; Sigma–Aldrich, Milwaukee, WI, USA) column chromatograph. Finally, tetrabutyltin (Sigma–Aldrich) was added to the concentrated eluants as a recovery standard. TBT, dibutyltin (DBT), and monobutyltin (MBT) concentrations were determined by gas chromatography equipped with a flame photometric detector (GC-FPD; 6890 series Agilent Technologies, Wilmington, DE, USA). A DB-5 capillary column (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness; J&W Scientific, Palo Alto, CA, USA) was used.

For quality assurance and quality control, analyses of procedural blanks, certified reference materials (NIES No. 11 [sea bass, Ibaraki, Japan; 0.47 ± 0.04 μg Sn/g as TBT]), and spiked samples were performed. Procedural blanks were processed in the same way as the samples. The blanks did not contain quantifiable amounts of the target compounds. The analytical results for NIES No. 11 ($n = 6$) were 0.41 ± 0.04 μg Sn/g as TBT. Recoveries of TBT, DBT and MBT spiked in sea sand ($n = 6$) were in the range of 73–122%. Limits of detection were calculated as three times the signal-to-noise ratio, 6–7 ng/g wet weight (wt) for MBT, DBT, and TBT.

Student's t-test was performed to investigate any significant differences in the concentration of BTs between the two cetacean species and their genders. The relationship between BT compounds and between the residue levels of BTs and body length in cetaceans was investigated using Spearman's correlation analysis. The SPSS version 11.0 software package for Windows was used for the statistical analysis.

Concentrations of BTs in the livers of minke whales and common dolphins from the Korean coast are summarized in Table 1. Total concentrations of BTs ranged from 15.7 to 297 ng/g wet wt for minke whales and from 59.0 to 412 ng/g wet wt for common dolphins. Concentrations of TBT, DBT, and MBT in the livers of the minke whales were in the ranges of less than limit of detection (<LOD)–55.9 ng/g wet wt, <LOD–215 ng/g wet wt, and <LOD–50.2 ng/g wet wt, respectively, while of the common dolphins were in the ranges of 29.2–85.7 ng/g wet wt, 5.92–257 ng/g wet wt, and 8.83–69.0 ng/g wet wt, respectively.

DBT was the main compound in BTs and its proportions accounted for 65 ± 23% (mean ± SD) for minke whales and 60 ± 12% for common dolphins. The proportion of TBT was 15 ± 11% for minke whales and 26 ± 8.1% for common dolphins. There are two possible reasons for being higher concentrations of DBT than TBT in our study. The first is that the liver detoxifies the parent compounds to metabolites; thus, TBT in the liver is transformed metabolically into by-products such as DBT and MBT (Lee, 1991; Kannan et al., 1997). Other studies have shown a higher proportion of degraded by-products than TBT in the livers of cetacean species (Table 2). The second reason is that the legislated ban on TBT in 2003 has decreased TBT in Korean waters (Choi et al., 2009a, 2010), suggesting that TBT has no on going source.

Spearman's correlation analysis showed that concentrations of MBT, DBT, and TBT in minke whales and common dolphins were significantly correlated with each other ($p < 0.0001$). Higher correlations were found between TBT and DBT ($r = 0.741$) and between DBT and MBT ($r = 0.719$), than between TBT and MBT ($r = 0.553$). This result could be a difference in metabolic rate for these compounds. Some studies reported that the metabolic rate of TBT to DBT is faster than that of DBT to MBT by cytochrome P450 enzymes present in the liver (Lee, 1991).

Although there was a limitation of different sampling periods for TBT contamination, the overall BT concentrations in the livers of cetaceans from Korean coastal waters were lower than those reported elsewhere (Table 2). This result is similar to the contamination status of BTs in the coastal environment of Korea compared with other coastal waters (Choi et al., 2009a,b, 2010). The mean concentration of BTs in cetaceans from Korea was much lower than those of killer whales, and finless porpoises from Japan (Harino et al., 2008; Nakayama et al., 2009), finless porpoises from Hong Kong (Nakayama et al., 2009), and harbor porpoises from Denmark (Strand et al., 2005). BT concentrations in Indo-Pacific humpbacked dolphins and bottlenose dolphins from India (Tanabe et al., 1998) and Atlantic spotted dolphins and pygmy sperm whales from the US (Kannan et al., 1997) are comparable to the BT concentrations measured in this study. Harbor porpoises from Greenland (Strand et al., 2005) and long-snouted spinner dolphins from the Philippines (Tanabe et al., 1998) showed lower levels of BTs than those in our study.

The concentrations of MBT, DBT, TBT and total BTs in the livers of common dolphins were significantly greater than those in minke whales (Fig. 1). It can be associated with differences in the habitat and diet between these two species of cetaceans. The common dolphin is a near-shore species feeding in coastal waters, whereas minke whales move between near-shore and off-shore habitats (Cho et al., 2003; An et al., 2004). Kannan et al. (1997) has reported that concentrations of BTs in bottlenose dolphins, occupying bays, estuaries and inshore channels between islands, are 3–4 times higher than those in off-shore species; i.e., spotted dolphins and pygmy sperm whales. The major prey of common dolphins is long-lived and larger predatory fish such as herring and mackerel

Table 1
Concentrations (ng/g wet wt) of butyltin compounds in the livers of minke whales and common dolphins collected from Korean coastal waters.

Species	Growth stage	MBT		DBT		TBT		ΣBT	
		Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Minke whale	Immature (M)[a]	8.40 ± 4.71	<LOD–14.0	29.8 ± 16.2	<LOD–46.0	14.2 ± 4.41	7.10–19.7	52.4 ± 19.1	21.1–73.8
(*Balaenoptera acutorostrata*)	Mature (M)	22.5 ± 14.9	<LOD–50.2	89.3 ± 35.8	57.8–158	11.7 ± 9.30	<LOD–27.5	123 ± 50.1	64.8–223
	Immature (F)[b]	14.1 ± 9.73	<LOD–30.5	68.6 ± 68.3	<LOD–215	17.6 ± 20.4	<LOD–55.9	100 ± 94.6	15.7–297
Long-beaked common dolphin	Mature (M)	35.6 ± 19.3	8.92–65.0	151 ± 46.5	88.7–236	60.3 ± 15.8	31.4–81.1	247 ± 71.9	139–377
(*Delphinus capensis*)	Mature (F)	26.8 ± 17.8	8.83–69.0	127 ± 67.3	5.92–257	51.0 ± 17.7	29.2–85.7	205 ± 96.9	59.0–412

[a] Male.
[b] Female.