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Baseline

PBDEs, methoxylated PBDEs and HBCDs in Japanese common squid (*Todarodes pacificus*) from Korean offshore waters

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ABSTRACT

Little information is available on the levels of brominated compounds found in biota from the Korean Peninsula. In this study, Japanese common squids (*Todarodes pacificus*) were analyzed for 38 polybrominated diphenyl ethers, two methoxylated polybrominated diphenyl ethers and three stereoisomers of hexabromocyclododecane (α, β, and γ-HBCD) from the east and western coasts of the Korean Peninsula. Among 38 PBDEs, 10 PBDEs were detected and their total concentrations ranged from 21 to 292 ng/g lipid wt with a mean concentration of 108 ng/g lipid wt, while two MeO-BDEs and three isomers of HBCDs were detected in all samples. BDE47 showed the highest residual level, followed by BDE99, 154, 153, 28/33. Concentrations of PBDEs and MeO-BDEs were not significantly different between the both sides of the Korean Peninsula; however, HBCD concentrations were higher levels in the East/Japan Sea than the Yellow Sea, indicating that HBCD sources possibly exist in Japan.

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are widely used as additive flame retardants in a wide range of products, such as polyurethane foam, upholstery textiles, and electric and electrical equipment. Their use has been increasing over the past few decades and this has been reflected by an increase in environmental levels (Norénm and Meironyté, 2000; Tanabe, 2008). PBDEs and HBCDs can enter the environment by a number of different pathways, such as emission during production of brominated flame retardants (BFRs), during the manufacture of products containing BFRs, and leaching during the usage and disposal of these products. Due to their physico-chemical and toxicological characteristics, which are similar to organochlorine compounds, there has been an increasing concern over the contamination of the environment from these brominated compounds and many studies have been conducted to monitor levels in various environmental and biological samples (Darnerud et al., 2001; Covaci et al., 2006; Tanabe, 2008; Stapleton and Dodder, 2008).

In order to evaluate the contamination of persistent organic pollutants (POPs) in Korean coastal areas, many studies have examined levels of POPs in coastal water, sediment, and biota including bivalves and fish (Kim et al., 2002; Hong et al., 2003; Yim et al., 2005; Hong et al., 2006). However, data on Korean offshore waters is sparse. Our group first reported POP levels on Korea offshore waters using Japanese common squid (*Todarodes pacificus*) (Won et al., 2009). Squid are a type of cephalopod, which generally have a short life (1–3 years), grow fast, have a spawning cycle, and are a predator located high in the food chain (Boyle and Knobloch, 1982). The Japanese common squid (*T. pacificus*) used for this study are born adjacent to the East China Sea (ECS), migrate to both sides (Yellow Sea and East Sea/Sea of Japan) of the Korean Peninsula for growth, and then return to ECS for spawning. They are caught easily around the Korean Peninsula. Thus, this species is a useful bioindicator of POPs pollution in offshore Korean waters.

Previous studies have compared PBDE levels in various areas off Coastal Asia using fish and marine mammals (Kajiwara et al., 2004; Sinkkonen et al., 2004; Tanabe, 2008; Isobe et al., 2009). However, these studies used different species, or used samples collected during different time periods, making it difficult to elucidate the difference in PBDE contamination between the different regions. Therefore, the objective of this study was to determine if the emerging contaminants, PBDEs and HBCDs, would be found in Japanese common squid collected during the same time period and determine if their levels are significantly different between the east and the west side of the Korean Peninsula.

Japanese common squids were collected from East Sea/Sea of Japan, and from the Yellow Sea, in August 2006 (Fig. 1) and frozen immediately. Their whole length and the weight of each organ were measured at a laboratory. In addition, liver was dissected and dried in a freeze-drying apparatus. All samples were wrapped with aluminum foil and kept in the freezer before chemical analysis. These squid are the same samples analyzed for chlorinated compounds by Won et al. (2009).

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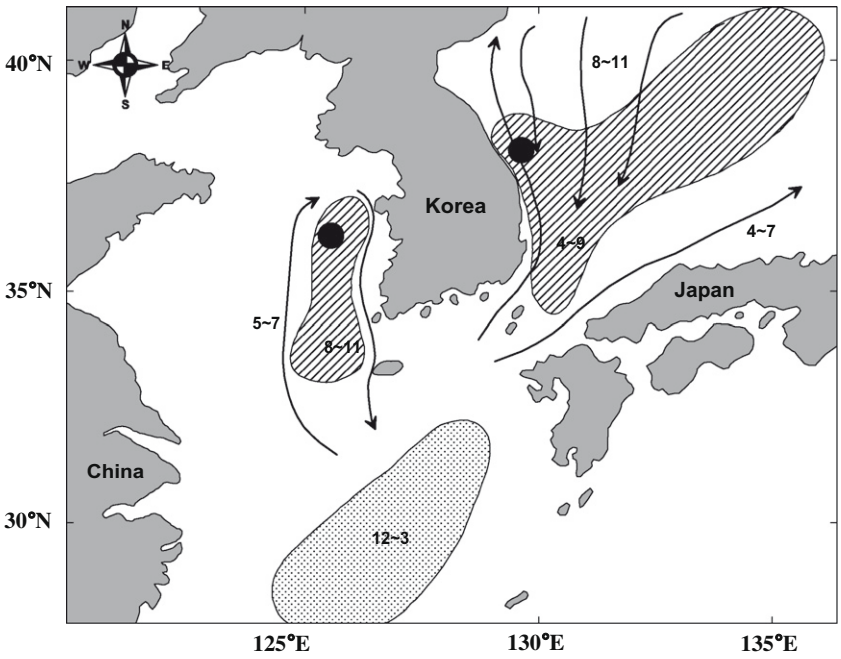

Fig. 1. Sampling locations (●) and migration route (—) of squid (*Todarodes pacificus*). (dotted area; spawning ground, dashed area; growing ground, number; the month of the year).

The method for analyzing 38 PBDEs and two MeO-BDEs in squid is a modification of the method reported by Stapleton et al.(2006). Samples were thawed and spiked with 50 ng of an internal standard, 4-fluoro-2,3,34,5,6-hexabromodiphenyl ether (FBDE160) and ^{13}C-BDE209 and then extracted via accelerated solvent extractor (ASE 300, DIONEX, Sunnyvale, CA, USA) using dichloromethane. Extracts were concentrated using a TurboVap (Cliper Life Science, Hopkinto, MA, USA) to 1.0 mL and then lipid residues were removed using gel permeation chromatography (GPC). Further clean-up was accomplished by eluting the extract through 8.0 g of Florisil deactivated with distilled water (2.5%). Prior to analysis on the GC/MS, 50 ng 4-fluoro-2,3,4,6-tetrabromodiphenyl ether (FBDE69) was spiked into the sample to measure recovery of FBDE160 and ^{13}C-BDE209(decabromodiphenyl ether). All samples were analyzed using gas chromatography mass spectrometry operated in electron capture negative ionization mode (GC/ECNI–MS). Extracts were routinely analyzed for a suite of 38 BDE congeners ranging from tri- to deca-BDE using a 5 point PBDE calibration standard. A 0.25 mm (I.D.) × 15 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (0.25 mm film thickness; J&W Scientific) was used for the separation of BDE congeners. Pressurized temperature vaporization (PTV) injection was employed in the GC. The inlet was set to 80 °C for 0.3 min and then a rapid 600 °C/min ramp to 275 °C was employed to efficiently transfer the samples to the head of the GC column. The oven temperature program was held at 80 °C for 1 min followed by a temperature ramp of 18 °C/min to 250 °C, followed by a temperature ramp of 1.5 °C/min to a temperature of 260 °C, followed by a final temperature ramp of 25 °C/min to 300 °C which was held for an additional 20 min. The transfer line temperature was maintained at 300 °C and the ion source was held at 200 °C. Tri- to nona-BDE congeners and both fluorinated BDE standards were quantified by monitoring bromide ions (*m*/*z* 79 and 81) using GC/ECNI–MS. BDE 209 and ^{13}C-BDE 209 were quantified by monitoring *m*/*z* 486.6/484.6 and 496.6/494.6, respectively. A laboratory blank was included in every batch and limits of detection (LOD) were determined by three times the standard deviation of the laboratory blanks. LODs ranged between 0.37 ng (BDE30) and 5.9 ng (BDE206). Recovery of FBDE160 averaged 53 ± 15%. Due to a relatively low recovery of FBDE160, all data in samples were corrected for blank and recovery. BDE209 in samples could not be calculated due to an extremely low recovery of ^{13}C-BDE209, surrogate for BDE209. In addition, the mean recoveries of 37 PBDEs in spiked blanks (n = 6) ranged from 80% to 101% except BDE206 with 42%. For the analysis of hexabromocyclododecane (HBCD), the final extracts were dried and reconstituted in methanol and then 50 ng of ^{13}C-HBCD (alpha isomer) was spiked into the sample as a quantification standard. LC–MS/MS was used for the determination of α-, β-, γ-HBCD. Samples were analyzed for α-, β-, γ-HBCD by LC/MS/MS (Agilent 6410, Agilent, Santa Clara, CA) on a Zorbax XDB-C18 column (4.6 × 50 mm, 1.8 μm) using negative ion electrospray ionization and detection by multiple-reaction monitoring (Stapleton et al., 2006). An isocratic mobile phase consisting of 90% methanol and 10% water was used at a flow rate of 400 μL/min. All three stereoisomers of HBCD were detected in all samples; any HBCD was not detected in lab blanks. HBCD levels were not corrected for recovery. Concentrations of all compounds were calculated based on lipid weight. Lipid content was determined by gravimetric analysis. Student *t*-tests and Pearson correlations were used to check the difference in concentrations of brominated compounds between the two study areas and to test the relationships among PBDE compounds.

Among 38 PBDEs, only ten PBDEs (eight peaks) were detected in squid samples higher than detection limits; BDE 30, 28/33, 75, 47, 99, 85/155, 154, 153. ΣPBDEs in squid (n = 14) from the East Sea ranged from 21 ng/g to 291 ng/g lipid wt with a mean concentration of 98 ng/g lipid wt, while those from the Yellow Sea (n = 13) showed a range between 33 ng/g and 211 ng/g lipid wt with a mean concentration of 118 ng/g lipid wt (Table 1). There was no statistical difference in PBDE concentrations between the sampling areas (Fig. 2(A)).

Won et al. (2009) reported using Japanese common squid from the Yellow Sea, on the western side of the Korean Peninsula, and found higher PCBs, DDTs, and HCHs concentrations compared with the East Sea/Sea of Japan located on the eastern side. This may indicate that China, with rapid industrial development, is a potential polluter to the Yellow Sea. In the case of organochlorines, many