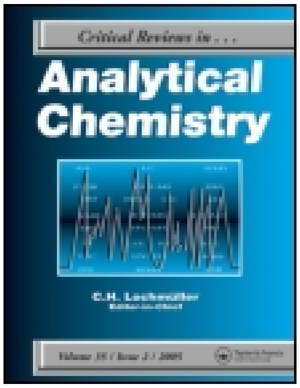

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Concentrations of polybrominated diphenyl ethers (PBDEs) in Kuwait's fish market have not previously been reported. Fish from four common species, shrimp, and five common shellfish from Kuwait's fish market were analyzed for seven PBDEs. The levels of PBDEs in fish samples ranged from 0.50 to 3.748 ng/g wet weight and in shellfish samples ranged from 1.05 to 5.47 ng/g wet weight. The mean σ_5 PBDE concentrations measured in hamoor, shell, zobaidy, sheim, shrimp, suboor, sponge, octopus, squid, and bivalve samples were 1.49, 5.47, 4.10, 0.50, 3.78, 1.53, 2.10, 3.11, 1.05, and 1.41 ng/g wet weight, respectively. The total PBDE concentration in fish and shellfish samples measured in our study were comparable to or higher than those from other countries. The BDE-47, BDE-99, and BDE-100 were the most dominant PBDEs in all the samples tested. The daily intake of PBDE from fish and shellfish reported in this study was lower than that reported from other countries.

Keywords polybrominated diphenyl ethers (PBDEs), fish, shellfish, Kuwait fish market, estimated daily intake

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs) that are used in a large variety of commercial and industrial products. They are widely used in the electronics, plastics, and textile industries and were the first group of BFRs to be detected in the environment (Alaee et al., 2002; Alaee and Wenning, 2002). Flame retardants are added to materials to prevent them from burning and to decrease the severity of a fire of a variety of products. They are useful when the flame retardancy of an objective technical polymer material is increased (Christensen et al., 2002). PBDEs can enter into the environment during the manufacture of these chemicals, by volatilization, leaching during use, and from an incinerator of municipal waste (Voorspoels et al., 2003). PBDEs are of environmental concern as they can affect the endocrine and neural system of humans and wildlife (Darnerud, 2008; Kim et al., 2006). These chemicals are persistent, potentially bioaccumulate, and can spread widely via the atmosphere (Mai et al., 2005). Penta- and oct-PBDEs are listed as persistent organic pollutants (POPs) and were restricted under the Stockholm Convention in 2009, while deca-BDE was banned by the EU in 2008 (De Wit et al., 2010). PBDEs have been found in a great variety of environmental media, such as fish (Cheung et al., 2008; Wu et al., 2009), marine mammals (Tanabe, 2007), birds (Norstrom et al., 2002), sediment (Gevao et al., 2006), and humans (Daniels et al., 2010; Zhu et al., 2009). Marine organisms are utilized for evaluating the quality of the marine environment as they are known to have a strong ability to accumulate POPs (Thomas and Charles, 2004). The status of the contaminant in biological samples needs to be clarified, since less information is available on the exposure of POPs for humans (Bi et al., 2002). In the past decade, there was a dramatic increase in temporal trends of PBDEs in humans and biota (Parmanne et al., 2006; Law et al., 2006). The PBDE trends emphasize that their levels in the environment should be monitored. Fish are considered to be the main route of human exposure to organic pollutants and have been utilized as an ideal biota for POPs monitoring (United Nations Environmental Programme, 2003). Bivalves are also used as bio-indicators of organic pollutants in marine environments; however, few studies have reported the levels of PBDEs in bivalves (Booiji et al., 2002; Gustaffon et al., 1999). Therefore, a wide group of fish and shellfish have been included in our study in order to obtain a clear prospective on PBDE accumulation.

Pressurized liquid extraction (PLE) is one of the most common extraction techniques, which depends on using elevated pressure to reach a higher temperature than the boiling

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point of the solvent. An automated Power-Prep/PLE extraction system along with an automated cleanup system (from FMS) was used to extract and purify the samples. The Power-Prep system was recently used on biotic environmental samples (Bjorklund et al., 2000; European Standard, 1996) and was used to clean up samples of low fat content (Focant et al., 2000). The FMS system was used extensively to clean up biological samples with low fat for PCDDs, PCDFs, and coplanar PCB compounds (Focant et al., 2001; Saulo et al., 2005). In the Power-Prep™ cleanup system a disposable silica column (6 g) was loaded to the system throughout the experiment to clean up the extracted sample. The removal of lipids was done using gel permeation chromatography (GPC) column.

The marine organisms in this study were divided into two groups: (1) fish, which includes four types (zobaidy, sheim, hamoor, suboor), and shrimp (rubyan) and (2) shellfish, which includes shell, sponge, octopus, squid, and bivalves.

The objective of the current study was (1) to determine the levels of total and individual PBDEs congeners in a variety of marine organisms collected from a Kuwait fish market, (2) to evaluate the intake of PBDEs related to fish and shellfish consumption, and (3) to validate the pressurized liquid extraction (PLE) method and the automated Power-Prep™ cleanup system for the analysis of PBDEs in fish and shellfish. Moreover, the current study was conducted to add new information on the levels of PBDEs in edible marine samples consumed by the population from a Kuwait fish market.

EXPERIMENTAL SECTION

Standards

PBDEs (EC-5103) contain the following congener numbers: 17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, and 209, which were obtained from Cambridge Isotope Laboratories. Five calibration standard solutions contained a mixture of the 14 PBDE congeners at concentrations that varied from 16 to 125 ng/mL for all congeners, except BDE-209, which varied from 64 to 512 ng/mL; internal standard mirex was spiked at 100 ng.

Chemicals and /Materials

All solvents were of pesticide-grade. Hexane and dichloromethane were supplied by Merck (Darmstadt, Germany). Nitrogen gas was used to concentrate the extract. Evaporator (Heidolph-Verwenden, Germany) and anhydrous sodium sulfate were purchased from Sigma in Steinhein-Germany. Bio-Beads SX-3 were purchased from Bio-Rad (200–400 mesh, Bio-Rad Laboratories GmbH, Munich).

Gas Chromatography-Mass Spectrometry Conditions

The quantification of PBDEs was performed on an Agilent 5973 inert mass selective detector, using an Agilent Technology 6890 network gas chromatography (GC) system coupled with a negative chemical ionization (NCI) ion source. The system was operated in selective ion monitoring (SIM) mode, and 1 μL of the extract was injected into the GC using auto-sampler split-less mode on a 15 m DB5-ms column (0.25 mm i.d.; 0.25 μm film thickness) with helium as the carrier gas. The oven program was as follows: 80°C for 2 min ramped at 25°C/min to 220°C, and 5°C/min to 315°C held for 10 min. The ion m/z 79 and 81 were monitored for all PBDE congeners, except ions m/z 484 and 486 for BDE-209, and 402 and 404 for mirex. The injector temperature was 250°C; ion source, 23°C; and auxiliary temperature, 300°C.

Marine Samples

Marine samples such as fish and shellfish were extracted using an automated PLE extraction system and cleaned by the automated Power-Prep™ system. Fresh samples (5 g) of each species were mixed with anhydrous sodium sulfate. Samples were collected from the local fish market in Kuwait.

PLE System

Automated Power-Prep/PLE extraction systems were used for the extraction. The stainless steel cell was supported with connected Teflon end cap and filter. The Power-Prep/PLE system is controlled by a means of a PC using DMS6000 software, which shows the temperature and pressure in real time. Pump, flow rate, solvent, time, valve state, and cooling during the extraction run were adjusted by programming the software. Extraction was carried out at a temperature above the solvent boiling point and under pressure that maintains the organic solvent in its liquid state, which maintains the solvent below the critical condition as well as the viscosities and solvation power. Under the selected conditions, the extraction efficiency was enhanced and the required solvent was minimized.

Automated Power-Prep™ System

Cleanup was performed on the Power-Prep™ system (FMS, Waltham, Mass., USA). The valves, pump, pressure modules, and flow were controlled automatically by computer software. The internal pressure was not allowed to exceed more than 35 psi and was monitored by pressure gauges. The system was made of three to six electrostatic valves driven by computer software. Valve modules (V1-V6) were responsible for the selection of solvent and column. The cleanup of PBDEs was done using a prepacked disposable silica column (6 g), obtained from FMS and packed with polytetrafluoroethylene (PTFE) tubes sealed in Mylar packaging. The solvent was placed on the solvent containers, and the elution behavior was automatically programmed to use 80 mL hexane and 50 mL solvent mixture of hexane and dichloromethane (1:1; v/v).

Gel Permeation Chromatography

The gel permeation chromatography column is a nondestructive cleanup column, based on molecular size separation. It is used to fractionate and to remove lipids in materials, which elute first from the column. Bio-beads S-X3 (12 g) were used to effectively remove the lipids and to successfully elute the PBDEs. A 100 mL amount of DCM:hexane (1:1; v/v) was used. Lipids were eluted in the first 45 mL, and PBDEs was eluted in the next 45–100 mL. The extract was taken for further cleaning with a pre-packed silica gel column to remove the small amounts of co-extracted impurities that might remain in the extract.

RESULTS AND DISCUSSION

Linearity of the Method

The linearity of the method for PBDEs was studied over a range of concentrations 16.25–125 pg/μL. The response was linear with correlation coefficient (r^2) > 0.991 for most of the compounds. The standard deviation of the retention times for PBDEs was calculated, and the results indicated that there were no clear deviations in retention time when matching the standard with the sample chromatograms (Table 1).

Repeatability and Reproducibility

Fresh fish and shellfish were spiked with standard PBDEs. Repeatability was evaluated by performing six replicates for PBDEs in the same day and under the same conditions. Reproducibility was evaluated by performing the analysis of one sample on three and four different days. The reproducibility for fish and shellfish with RSD ranged from 9.2 to 18.5%, and for RSD ranged from 12.5 to 19.6%. The overall results showed that the quantification method was accurate and precise.

Matrix Effect

The fresh weight fish and shellfish samples were spiked with a known concentration of PBDEs, while at the same time one unspiked sample was also extracted along with a procedural blank sample. The matrix effect was evaluated in order to determine if there was any effect on the analyzed concentration. The results showed that there were no matrix effects on PBDEs congeners.

TABLE 1
Calibration data and correlation coefficients for PBDEs

PBDEs	Calibration range (pg/μL)	Correlation coefficient (r^2)	LOD (ng/g)	LOQ (ng/g)
47	16.25–125	0.997	0.22	0.66
100	16.25–125	0.994	0.04	0.12
99	16.25–125	0.994	0.13	0.39
154	16.25–125	0.993	0.15	0.45
153	16.25–125	0.991	0.19	0.57

Limit of Detection (LOD) and Limit of Quantification (LOQ)

LOD and LOQ were determined at the residual levels (ng/g), corresponding to a signal-to-noise ratio of 3 for LOD and 10 for LOQ. The method detection limits were in the range of 0.04–0.19 ng/g (wet weight) and the quantitation limits varied from 0.12 to 0.57 ng/g (wet weight) (Table 1).

Levels of PBDEs in Fish and Shellfish

The results obtained for PBDEs in fish and shellfish from a Kuwait fish market are listed in Table 2. The English, local, and scientific names of the fishes are summarized in Table 3. Concentrations of BDE-47, BDE-99, and BDE-100 were the highest predominant congeners of BDE in most of the species analyzed. Bromodiphenyl ethers (BDE-47), BDE-99, and BDE-100 accounted for approximately 90% of the total level of PBDEs in aquatic biota (Jansson et al., 1993; Asplund et al., 1999), and BDE-47 accounted for more than 60% of the total levels of PBDEs (Jansson et al., 1993). Concentration of the $\sum$PBDEs individual congeners ranged from 0.10 to 4.8 ng/g (wet weight) and from 0.39 to 5.18 ng/g (wet weight) for fish and shellfish samples respectively. Total PBDE levels were expressed as a sum of five PBDE congeners and they are as follows: 1.49, 5.47, 4.10, 0.50, 3.78, 1.53, 2.10, 3.11, 1.05, and 1.41 ng/g (wet weight) for hamoor, shell, zobaidy, sheim, shrimp, suboor, sponge, octopus, squid, and bivalve, respectively. The overall total concentrations ($\sum$PBDEs) of the samples ranged from 0.50 to 3.78 ng/g (wet weight) and from 1.05 to 5.47 ng/g (wet weight) for fish and shellfish, respectively. BDE-47, BDE-99, and BDE-100 were the most dominant PBDE congeners detected in the samples. The overall percentage of BDE-47, BDE-99, and BDE-100 were found to be more than 90% in most of the samples.

Their percentage levels in fish and shellfish are presented in Figure 1, which shows that the congeners in the penta-BDE mixture are highly bio-accumulated. The congeners BDE-47, BDE-99, and BDE-100 are dominant congeners in technical penta mixture (Sjodin et al., 1998). BDE-153 and BDE-154 are detected in four out of ten samples, and their concentrations were close to the detection limits.

Concentrations of the total PBDE individual congeners and their percentage of distribution in fish and shellfish are given in Table 4. Congener concentrations in fish and shellfish from high to low were as follows: BDE-47 > BDE-99, BDE-100 > BDE-154 > BDE-153. In this study, the five congeners accounted for 41%, 30.77%, 22.2%, 1.97%, and 1.45% for BDE-47, BDE-99, BDE-100, BDE-154, and BDE-153, respectively of the total concentrations (Table 4). However, the five congeners in shellfish accounted for 39.42%, 35.69%, 16.8%, 5.1% and 2.97% of the total concentrations, respectively (Table 4). The same five congeners accounted for 69.1%, 15.4%, 12.8%, 12.8, 4.8%, and 2.8% of the total PBDEs concentration in fish from Europe (Hites, 2004). The overall PBDEs congeners in fish accounted for 68%, 4.1%, 3.2%, 6.7%, 12.0%, and 1.3% for BDE-47,

TABLE 2a
Total concentration of PBDEs in fish and shellfish samples collected from Kuwait fish market

PBDEs	Hamoor mean± SD (n = 4)	Zobaidy mean, ±SD (n = 5)	Sheim mean, ±SD (n = 2)	Shrimp mean, ±SD (n = 2)	Suboor mean, ±SD (n = 2)
47	1.15 (1.44)	1.70 (1.53)	0.22 (0.31)	1.21 (1.14)	0.52 (0.09)
100	0.15 (0.30)	1.10 (0.91)	0.16 (0.22)	0.72 (0.61)	0.47 (0.19)
99	0.19 (0.38)	1.30 (1.21)	0.12 (0.17)	1.45 (1.27)	0.54 (0.39)
154	n.d.	n.d.	n.d.	0.23 (0.32)	n.d.
153	n.d.	n.d.	n.d.	0.17 (0.24)	n.d.
∑PBDE	1.49	4.10	0.50	3.78	1.53

TABLE 2b
Total concentration of PBDEs in fish and shellfish samples collected from Kuwait fish market

PBDEs	Shell mean, ±SD (n = 12)	Sponge mean, ±SD (n = 5)	Octopus mean, ±SD (n = 4)	Squid mean, ±SD (n = 2)	Bivalve mean, ±SD (n = 2)
47	2.01 (1.42)	1.15 (0.52)	1.31 (0.86)	0.34 (0.17)	0.37 (0.22)
100	0.71 (0.33)	0.32 (0.32)	0.41 (0.49)	0.35 (0.05)	0.42 (0.05)
99	2.11 (1.48)	0.63 (0.63)	1.15 (1.26)	0.36 (0.07)	0.44 (0.25)
154	0.35 (0.32)	n.d.	0.14 (0.28)	n.d.	0.18 (0.25)
153	0.29 (0.34)	n.d.	0.10 (0.20)	n.d.	n.d.
∑PBDE	5.47	2.10	3.11	1.05	1.41

BDE-99, BDE-100, BDE-153, BDE-154, and BDE-3, respectively of the total PBDEs concentrations in pomfret and 47.8%, 8.3%, 8.3%, 4.5%, 15.2% and 10.4% of the total PBDEs concentration in yellow croakers, respectively (Xia et al., 2011).

It is interesting to note that lower levels of BDE-28 and BDE-71, which were usually not detected in other studies, were detected in this study in zobaidy fish with concentrations close to the detection limits. In another study, lower levels of BDE-15 and BDE-28 were found in sediment (Chen et al., 2006) and human breast milk from China (Sudaryanto et al., 2007). Tetra-BDE product was used in Japan until 1990 but is no longer commercially produced (Akutsu et al., 2001). BDE-209 was not detected in any fish and shellfish samples. This can be explained by the fact that BDE-209 is not bio-available to

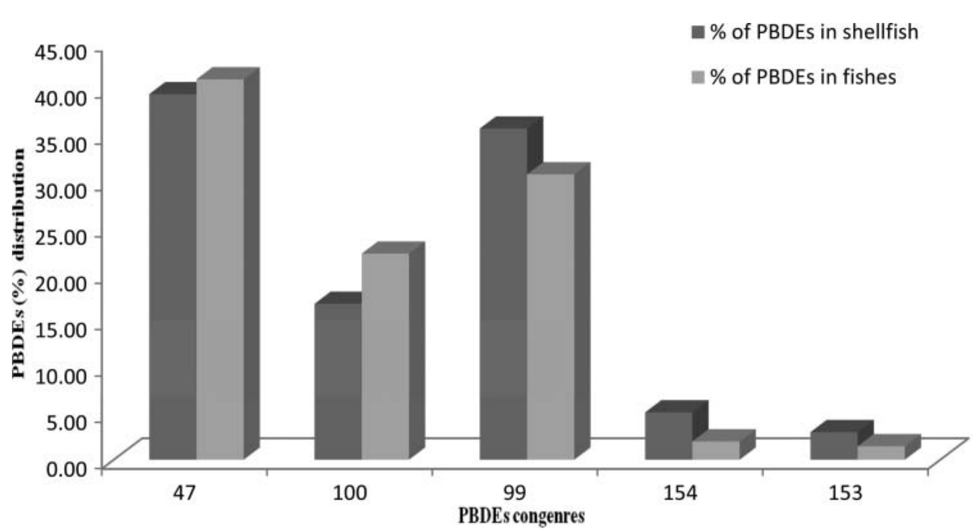

FIG. 1. Total distribution percentage (%) of PBDE congeners in fish and shellfish.

TABLE 3
English, local, and scientific name of the fish tested in this study

English name	Local name	Scientific name
Silver pomfret	Zobaidy	*Pampus argentens*
Yellow seabream	Sheim	*Acanthopagus latus*
Orange-spotted grouper	Hamoor	*Serranidae*
Hilsa shad	Suboor	*Tennalosail isha*
Jinga shrimp	Rubyan	*Meta penanes*

marine aquatic organisms because of their large molecular size (Hardy, 2000) and large octanol/water partition coefficient (10 gkow∼10). BDE-209 also has lower bio-availability compared to other BDE congeners (Meng et al., 2007), which could be linked to the photolytic debromination in the environment or to their scarcity in the Middle East (Bondi et al., 2010). Bondi et al. (2010) observed the absence of high molecular weight BDE congeners in sediment samples (Gevao et al., 2006). The predominance of BDE-47, BDE-99, and BDE-100 in aquatic organisms (fish and shellfish) shows their primary exposure to penta-BDE, and that they are the most bio-accumulative congeners from the commercial penta-BDE mixture (Oros et al., 2005). The ∑PBDEs concentration in the fish group shows that the yellow pomfret (zobaidy) had the highest concentration, followed by hilsa shad (suboor), orange-spotted grouper (hamoor), sea bream (sheim), and jinga shrimp (rubyan).

The ratio of the percentage of distribution for BDE-47 and BDE-99 is 1.1 in a technical penta formulation, Bromkal 70–5DE (Sjodin et al., 1998). In our study, the ratio was 1.1 and 1.33 for fish and shellfish, respectively. The predominance of these compounds could be a result of physicochemical properties (Bondi et al., 2010). An interesting trend is obtained when the ratio of BDE-99 and BDE-100 was compared. In this study, the ratio of BDE-99 and BDE-100 was found to be 58:42 and 68:32 for fish and shellfish, respectively. The similar ratio of BDE-99/BDE-100 in fish (silver promfret and yellow croaker) from eastern China was also observed (Xia et al., 2011). In air and sediment, the ratio of BDE 99/100 was 80:20 (Dodder et al., 2000), which is similar to the ratio in industrial product Bromkal 70–5DE (Sellstorm et al., 1998; Christensen and Platz, 2001). This can be due to higher bioavailability of BDE-100 or less biodegradability of BDE-100 than BDE-99 (Christensen et al., 2002). The distribution trend of congeners (BDE-47/BDE-99) found in biological samples suggests that it is linked to the composition of penta-BDE commercial product (De Boer et al., 2000). However, such congener profiles in fish, BDE-47 and BDE-99, dominated, reflecting primarily penta-BDE (Cheung et al., 2008). The present values were higher than those of fish from the U.S., which varied from 0.001 to 3.73 ng/g wet weight (Schecter et al., 2006), and those from Japan, which varied from 0.018 to 1.72 ng/g wet weight (Ohta et al., 2002) (Table 5). The total PBDE concentrations in fish and shellfish samples investigated in our study were comparable to or higher than those from other countries. Concentrations of ∑PBDEs in fish from Hong Kong ranged from 7.29 to 13.2 ng/g wet weight (Cheung et al., 2008), and in mussels from the Netherland from 1.2 to 28 ng/g wet weight (De Boer et al., 2003). These concentrations found in fish and shellfish species were lower than the results found in this study.

TABLE 4
Concentration of the total PBDE individual congeners and their percentage (%) distribution in fish and shellfish sample

	Total PBDE congeners	Total PBDE congeners	Total PBDE congeners	
PBDEs	Fish	PBDEs (%)	Shellfish	PBDEs (%)
28	0.2	1.71	n.d.	n.d.
71	0.1	0.85	n.d.	n.d.
47	4.8	41.03	5.18	39.42
100	2.6	22.22	2.21	16.82
99	3.6	30.77	4.69	35.69
154	0.23	1.97	0.67	5.10
153	0.17	1.45	0.39	2.97
∑PBDEs	11.7		13.14	

Intake Estimation

Fish is a food in high demand as it has high nutritional value. Several authors have pointed out that the persistent organic pollutant (POPs) contaminants mean that they could be a potential health hazard. The lipid content in fish varies considerably in different portions of tissue in fish; therefore, it is important to check the uptake of PBDEs in fish. However, the amount of PBDEs and other POP components should be limited in the human diet (Stern, 2007; Domingo et al., 2007). The European Food Safety Authority (EFSA) has recommended a method for risk limitation from the consumption of foods contaminated with PBDEs, which can be evaluated based on the provisional tolerable weekly intake (PTWI). The value for PBDEs was 0.7 μg/kg body weight (European Food Safety Authority, 2005), equaling 49000 ng for an adult weighing 70 kg for a weekly intake, which EFSA considers to be a less robust value. An average of 66.4 g/daily consumption rate of fish and shellfish in Kuwait was taken into account.

The estimated daily intake in the present study was calculated by multiplying the average concentration (ng/g wet weight) with the consumption rate of 66.4 g/day. Daily PBDE intake in the current study ranged from 0.53 to 4.37 ng/day for fish, 4.03 ng/day for shrimp, and 1.12 to 5.83 ng/day for shellfish. These values were lower than the daily intake of fish in other countries (Table 6).

TABLE 5
Total concentration of PBDEs found in fish and shellfish samples compared with other international studies (ng/g wet weight)

Location	∑PBDEs[a]	n[b]	Sampling year	References	Target species
USA	0.011–3.73	13	2006	Schecter et al., 2006	Herring, canned tuna, catfish, salmon, trout, etc.
Japan	0.018–1.72	6	2002	Ohta et al., 2002	Salmon, tuna, and yellowtail
Hong Kong	7.29–13.2	22	2008	Cheung et al., 2008	Yellow croaker, orange-spotted grouper, etc.
The Netherlands	1.2–28	5	2001	De Boer et al., 2003	Mussels
San Francisco Bay, USA	9–106	3	2002	Oros et al., 2005	Mussels, oysters, and clams
Kuwait	0.50–5.47	5	2010	Present study, Helaleh et al.	Fish, shell, shrimp, octopus, sponge, bivalves, and squid
Kuwait	(1) 0.196–10.56 (2) 0.497–9.19	4	2010	Bondi et al., 2010	(1) Seabream—Kuwait Bay (2) Seabream—Open Gulf
Hong Kong	0.38–9.19	20	2007	Moon H.-B. et al., 2007	Bivalves

[a]∑PBDE = sum of the target PBDE congeners
[b]number of PBDEs congeners analyzed in the samples.

TABLE 6
Estimated daily PBDE intake through selected fish and shellfish samples by people in Kuwait compared with other countries

		EDI* (ng/ day)						
Species	Average conc. (ng/g wet wt.)	Kuwait	USA	Belgium	Finland	Sweden	Spain	Hong Kong
Fish	1.95	0.53–4.37	8.94–15.7	14	23	23.1	20.8	514–931
Shrimp	3.78	4.03						
Bivalves, octopus, squid, shell, sponge	2.63	1.12–5.83	—	—	—	—	—	—
References		Present study	Schecter et al., 2006	Voorspoels et al., 2007	Kiviranta et al., 2004	Darnerud et al., 2006	Domingo et al., 2007	Cheung et al., 2008

CONCLUSION

The total PBDE concentrations in fish and shellfish ranged between 0.50 to 3.78 ng/g wet weight and 1.05 to 5.47 ng/g wet weight for fish and shellfish, respectively. The PBDE concentrations in fish were comparable to or higher than those obtained from other international regions of the world. BDE-47 and BDE-99 were found to be the predominant congeners in the fish collected from a Kuwait fish market. This observation enhances the evidence that the use of penta-BDE was considered to be the main PBDE contamination source. The estimated daily PBDE intake through fish and shellfish obtained in the present study was lower than those reported from other countries.

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