ASSESSMENT OF CURRENT SERUM LEVELS OF PBDEs IN AN URBAN POPULATION OF KOREA

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of synthetic chemicals widely used as flame retardants that are added to polymer resins and plastics, including electronic enclosures and polyurethane foam used in upholstery cushioning and carpet pads (De Wit, 2002; Alaee, 2003). PBDEs are considered persistent organic pollutants (POPs), because these chemicals are ubiquitously detected in the environment, and resistant to degradation, and accumulated in both wildlife and human due to their lipophilic properties. The global market demand has increased steadily in the past 30 years.

PBDEs have been detected in human serum, breast milk, and adipose tissues of almost all individuals regardless of age, sex, race, and region (Sjödin et al., 2003; Wang et al., 2007; Lorber, 2008). The general population of South Korea showed the highest serum PBDE concentrations compared to those have been reported in European and Asian countries (Wang et al., 2007).

PBDEs are present in many critical exposure media, including various foods, indoor air and house dust. In the general population, the major routes of human exposure to PBDEs are dietary intake of contaminated food and inhalation of contaminated indoor dust (Domingo, 2004; Wilford et al., 2005; Schecter et al., 2006b). PBDE levels in mother's breast milk were correlated with their house dust concentrations (Wu et al., 2007). Whereas, PBDE levels in urban anglers were higher than those of non fish-eating consumers (Morland et al., 2005) and high consumers of sportfish were found to higher levels of PBDEs compared with low consumers (Spliethoff et al., 2008). The relative contribution of pathways may also vary between countries and between congeners (Sjödin et al., 1999; Meng et al., 2007; Sjödin et al., 2008a).

In the present study we reported the results of PBDE measurements to evaluate current serum concentrations of PBDEs in an urban population with relation of MSWIs in Korea.

Subjects and Methods

Subjects and sample collection

Blood samples were collected from the volunteers who participated in the Health Assessment Study of Seoul Citizen related to municipal solid waste incinerators (MSWIs). The subjects were comprised of MSWIs' workers (n=8), nearby residents (n=41) living within 0.3 km of the MSWIs, and controls (n=10) who were not related the MSWIs. All participants lived in three areas (Kangnam, Nowon, Yangchun) of Seoul.

Analytical methods

Briefly, serum samples (4 g) were spiked with $^{13}C_{12}$-labeled surrogate standards (EO-5277, CIL, USA). The serum samples were denatured and diluted with an equal amount of formic acid (Aldrich, USA) and deionized water. The sample was then loaded onto the OASIS HLB (500 mg) cartridge (Waters, USA) and then eluted through the cartridge. Each cartridge was dried with nitrogen flow. The extract was applied to custom-made acid silica SPE cartridges packed with 100 mg of silica and 1000 mg of sulfuric acid silica, and then eluted with 12 mL of hexane through the cartridge Before the analysis, the samples were reconstituted with a $^{13}C_{12}$-labeled recovery standard (EO-5276, CIL, USA).

GC-HRMS analysis were performed on a JMS-800D instrument (JEOL, Japan) interfaced with an Agilent 6890N gas chromatograph (Agilent Technologies, USA). Total lipids were calculated using the formula (Phillips et al., 1989): Total lipids (mg dL^{-1}) = 2.27 × total cholesterol + triglycerides + 62.3. Total cholesterol and triglycerides were determined using an enzymatic assay method with ADVIA 1650 (Bayer, USA).

Quality control

For batch analysis, one procedure blank consisting of deionized water and one in-house reference material consisting of pooled human serum were analyzed for every ten samples analyzed. The isotope dilution method was used for PBDE determinations. Samples were spiked with $^{13}C_{12}$-labeled internal standards ($^{13}C_{12}$-BDE28, $^{13}C_{12}$-BDE47, $^{13}C_{12}$-BDE99, $^{13}C_{12}$-BDE100, $^{13}C_{12}$-BDE153, $^{13}C_{12}$-BDE154, $^{13}C_{12}$-BDE183, and $^{13}C_{12}$-BDE209) before extraction and with a $^{13}C_{12}$-labeled recovery standard ($^{13}C_{12}$-BDE139) before GC-HRMS analysis.

Data analysis

Total PBDEs (ΣPBDEs) were equivalent to the sum of PBDE congeners 28, 47, 99, 100, 153, 154, and 183. All statistical analyses were conducted using the SPSS 12.0 program. *p* values less than 0.05 were considered to be statistically significant. Relationships of investigated chemicals with demographics and possible exposure variables were examined using non-parametric statistical methodology. Correlation between PBDE congeners and other organochlorine residues and age was tested using the Spearman correlation coefficients of determination.

Results and discussion

Distributions of PBDE concentrations and congener profiles

The serum concentrations of seven PBDE congeners were measured in fifty nine individual serum samples from an urban population of Korea in 2006. The total PBDE concentrations ranged from 0.78 to 30.4 ng g^{-1} lipid. The average and median total PBDE concentrations were 5.31 and 3.86 ng g^{-1} lipid, respectively. Among the quantified BDE congeners, the most predominant congeners were BDE-153 accounting for 37.8 ± 21.3% (mean ± standard deviation) of total PBDEs, followed by BDE-47 (28.9 ± 19.6 %), BDE-100 (18.9 ± 10.1%), and BDE-99 (7.3 ± 10.2%). The BDE-183, which is the primary congener of the octa-BDE formulation, was lower than the average LOD of BDE-183 in all serum samples. The serum PBDE congeners profile showed large proportion of BDE-153. It was apparently seen that an increased proportion of BDE-153 in maternal serum samples from South China (Bi et al., 2006). The high concentration of BDE-153 in serum suggests that BDE-153 was poorly metabolized or highly persistent in human. In animal experiments, BDE-153 was less absorbed than BDE-47 and BDE-99, probably because of its larger size (Sanders et al., 2006).

Comparisons with various other studies

According to the recently published data, typical serum total PBDE concentrations from the United States were 30-80 ng g^{-1} lipid, while the serum total PBDE concentrations from Europe and Asia were less than 10 ng g^{-1} lipid (Lorber, 2008). The serum concentrations of PBDEs in our study were consistent with those found in the general population from Spain (Gómara et al., 2007), Sweden (Meironyté et al., 2003; Weiss et al., 2006), the United Kingdom (Thomas et al., 2006), Norway (Thomsen et al., 2002), New Zealand (Harrad and Porter, 2007), Japan (Takasuga et al., 2004) and China (Bi et al., 2006). Those countries showed that the median total PBDE concentrations ranged from 2.13 to 9.10 ng g^{-1} lipid.

The serum PBDE concentrations found in this study was much lower than those of previous our results (Kim et al., 2005; Lee et al., 2007). These two previous studies showed the mean PBDE concentrations for the general population were 14.9 and 15.1 ng/g lipid, respectively, which were approximately three times greater than those found in this study. In addition, BDE-183 was detected in previous serum samples with the mean concentrations of 2.83 and 2.07 ng g-1 lipid, respectively.

Correlations between PBDE concentrations and demographic factors

Serum PBDE concentrations in male were relatively higher than in females, but Mann-Whitney U test revealed that only concentrations of BDE100 were statistically significant ($p<0.05$). Age was the most significant and positive correlate of organochlorine contaminants in human serum (Kang et al., 2008), but age was not significantly correlated with any of PBDE congeners and total PBDEs in this study. We observed a linear increase of PBDE concentrations to the age 50-59 years old and then decreased over 60 years old. The highest levels in 50-59 years old could be explained by bioaccumulation through dietary intake or inhalation of contaminated house dust and longer time to contact compared the other age groups.

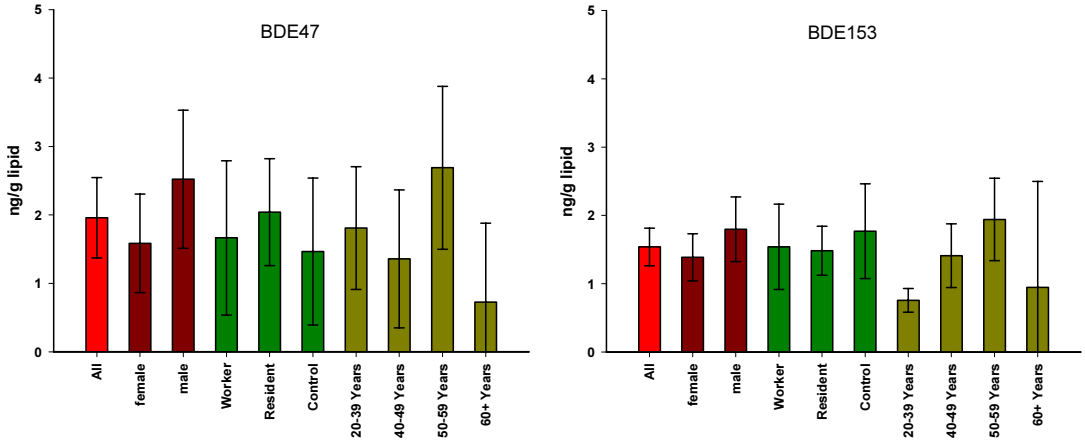

Figure. Mean concentrations and standard deviation (ng g^{-1} lipid) of (a) BDE-47 and (b) BDE-153 by gender, occupation, and age

Exposure source of PBDEs

The subjects in this study could be divided into three groups; incinerator workers from three MSWIs in Seoul, residents who lived in the vicinity of MSWIs (within 0.3 km), and controls who resided at long distances from the MSWIs (10 km away). Taking into account the results of this study in human serum samples, we can expect that incinerator workers were not exposed to PBDEs from their working places during incineration of wastes. In addition, we found the similar results that the concentrations of PBDEs in milk from women living in the vicinity of a hazardous waste incinerator (HWI) in Catalonia, Spain are similar or lower than the concentrations of PBDEs in milk reported in a number of recent other studies (Schuhmacher et al., 2007). Therefore, it seems that MSWIs cannot be a significant source of PBDE exposures for the general population living in close to MSWIs as well as the workers if they have proper protecting gears.

Correlation of PBDE congeners with organochlorine contaminants

Highly significant correlations were found between individual OCPs, PCBs, and PBDEs as well as between OCPs PCBs, and PBDEs. BDE 47 was significantly and positively correlated with p,p'-DDE and p,p'-DDT. BDE-153 was correlated with HCB, oxychlordane, trans-nonachlor, p,p'-DDE, p,p'-DDT, PCB153, and PCB187. However, BDE153 was not correlated with any other BDE congeners significantly. The relationship between OCPs and PCBs was substantially stronger than the relationship between PBDEs and OCPs or PCBs. In the NHANES 2003-2004 showed the significant relationship between DDE and total PBDEs (r = 0.26) (Anderson et al., 2008).

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