

Spatial Distribution, Temporal Variation and Health Risk Assessment of Brominated Flame Retardants in Human Breast Milk from Ghana

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Introduction

Brominated flame retardants (BFRs) constitute a diverse group of compounds mainly used to prevent or minimize the extent of a fire. The representative additive flame retardants, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are widely used in plastics, furniture, textiles and electronics such as computers, DVDs and TV-sets. Due to their environmental stability, persistence and high production volume, PBDEs and HBCDs are among the most abundant BFRs detected in the environment, wildlife and in humans (Alaee et al. 2003). Both are lipophilic, hydrophobic and have the propensity to bioaccumulate and biomagnify in food chains. The main sources of human exposure to PBDEs are through floor dust and food consumption (Sjoedin et al. 2008). Although several studies on environmental pollution by these persistent compounds have been reported in developed countries, less information is available in most developing countries, particularly in Africa. There is no production of BFRs in Ghana. However, the country is at the receiving end of electronic and electrical equipment or their wastes imported or dumped from developed countries. The aims of the study were therefore to elucidate the contamination status of PBDEs and HBCDs in human breast milk from Ghana, and assess health risk associated with the intake of contaminants by infants through breast milk consumption.

Materials and Methods

Human breast milk samples from primiparous mothers were collected from various locations in Ghana in 2004 and 2009. The informed consent was obtained from all the donors in an ethical manner. All participants completed a detailed questionnaire on age, weight, height, dietary habits and other data. The frozen samples were airlifted to the Center for Marine Environmental Studies (CMES), Ehime University, Japan on dry ice and kept in the Environmental Specimen Bank (*es*-BANK) of Ehime University at -25°C (Tanabe 2006) until chemical analyses. Forty-six samples, ($n=25$) from Accra in 2004, and ($n=21$) in 2009, made up of Accra ($n=8$), Kumasi ($n=6$) and Tamale ($n=7$) were used in analyzing for PBDEs and HBCDs. Accra, the capital of Ghana is the largest city followed by Kumasi in terms of industrial establishments and infrastructural development. Briefly, about 50g of the human milk sample was lyophilized and extracted with a solvent extractor using 50% acetone in hexane. Fat content was determined gravimetrically from an aliquot of the extract. The remaining extract was spiked with 5 ng of ¹³C₁₂-labeled BDEs and 10 ng of ¹³C₁₂-labeled HBCDs (α -, β -, γ - isomers) as surrogates and then subjected to gel permeation chromatography (GPC) for fat removal and eluted with a mixture of 50% hexane/dichloromethane (1:1). The lipid-removed GPC fraction containing organohalogen compounds

was concentrated and passed through 4 g of activated silica gel packed in a glass column. The first fraction containing PBDEs was eluted with 5% dichloromethane in hexane and the second fraction containing HBCDs with 25% dichloromethane in hexane for clean-up. $^{13}\text{C}_{12}$ -labeled BDE-(126+205) was added to the PBDEs fraction and deuterated HBCDs were added to the HBCDs fraction as internal standards.

Quantification of PBDEs was performed using a gas chromatograph coupled with a mass spectrometer (GC-MS). All the congeners were quantified using the isotope dilution method to the corresponding $^{13}\text{C}_{12}$ -labeled congeners. Forty BDE congeners from mono- to deca-BDE were analyzed in this study. HBCD isomers (α -, β -, γ -HBCD) were quantified using a liquid chromatograph coupled with a tandem mass spectrometer (LC-MS/MS). Concentrations of all the targeted BDE congeners and HBCD isomers were summed to obtain the values of Σ PBDEs and Σ HBCDs, respectively. Concentrations of PBDEs and HBCDs were expressed as nanogram per gram lipid weight (ng/g lw). For quality assurance/quality control (QA/QC), procedural blanks for every 7 samples were performed to check for any contamination during sample processing. Recoveries and instrument performance were checked using internal standards.

Results and Discussion

Residue levels and contamination status of PBDEs and HBCDs

Seventeen PBDE congeners from di- to deca-BDE were detected (Fig. 1). The concentrations of the sum of the 17 congeners (Σ PBDEs) found in all the breast milk samples from the three locations in 2009 ranged from 0.86 to 9.1 ng/g lw with an overall mean value of 3.6 ng/g lw. The range of concentrations were; Accra (1.3 – 9.1 ng/g lw, mean of 4.3 ng/g lw), Kumasi (0.89 – 6.7 ng/g lw, mean of 3.9 ng/g lw) and Tamale (0.86 – 4.9 ng/g lw, mean of 2.4 ng/g lw). Statistical differences were found for only BDE-100 between Accra and Tamale ($p=0.006$), and Kumasi and Tamale ($p=0.035$), as well as BDE-196 ($p=0.022$), BDE-206 ($p=0.008$) and BDE-208 ($p=0.022$) between Kumasi and Tamale. The highest concentration of Σ PBDEs (9.1 ng/g lw) in the breast milk was found in a 20-year old mother from Accra.

Among the PBDEs, BDE-47, -209, -99, -100, -(197+204) and -183 in that order were the dominant congeners (Fig. 1). BDE-47 was found to be the predominant congener in the samples in accordance with other studies dealing with human matrices, such as breast milk (Malarvannan et al. 2009; Daniels et al.

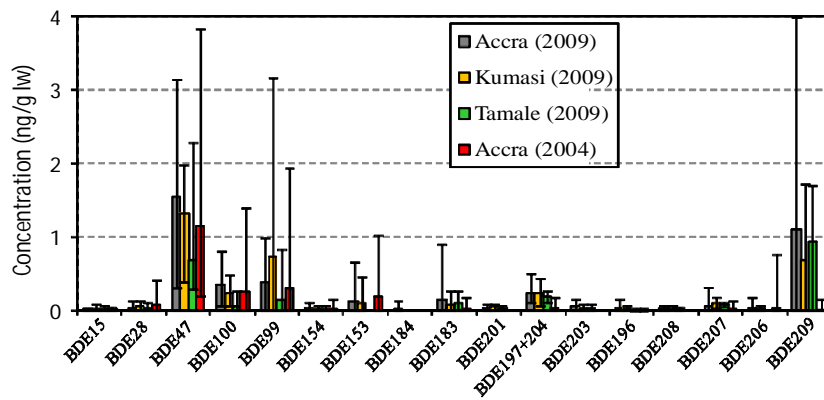


Figure 1. Levels and congener profile of PBDEs in breast milk samples from Ghana.

2010) and blood plasma (Mazadai et al. 2003). Interestingly, BDE-209 was found in some donors with concentrations higher than BDE-47. BDE209 has become controversial in recent years because of increasing evidence of its tendency to break down into lower brominated congeners in the environment, as well as within the bodies of biota (Betts 2008). This study reveals the exposure of certain people to higher brominated

BDEs which generally, have been observed in occupationally-exposed workers such as electronic dismantling and rubber factory workers (Sjoedin et al. 2003). The half-life of BDE-209 is short, estimated in the range of a week. The short half-life of BDE-209 indicates a quite rapid metabolism and debromination of BDE-209 into lower congeners. Thus, BDE-183, -197 and -207 found in this study could possibly be due to the debromination processes of BDE-209. Interestingly, the levels of PBDEs in this study were higher than some studies in Japan, some Asian and European countries (Malarvannan et al. 2009) but lower than in Canada (Ryan et al. 2002) and USA (Johnson-Restrepo et al. 2007).

Various sources of exposure to PBDEs, including meat, chicken, pork and fish appear to be important and common pathways for these contaminants. The diets of Ghanaians are predominantly mixed and comprise of the above listed items, among others. Furthermore, Ghana is a coastal country and people consume a lot of sea fish including herrings, tuna, salmon, red fish and octopus and could be one of the reasons for the high proportion of BDE-47 (Ueno et al. 2004). Recent studies have however shown that house dust contributes significantly to the exposure route of PBDEs in the general population because it is used as an additive to retard fire and flames in a variety of commercial and household products (Stapleton et al. 2008). For example, Lober (2008) showed that about 66% of the overall estimated intake of PBDEs in US was through house dust. Probably, dust could explain the high levels found in the present samples. Coupled with that, the style of eating in Ghana (generally by hand) could also contribute to the levels, especially if hands are not washed properly (Stapleton et al. 2008). However, since there have been no studies in Ghana on the accumulation of PBDEs in food and house dust, it is difficult to identify the major pathway to nursing mothers, at least for now.

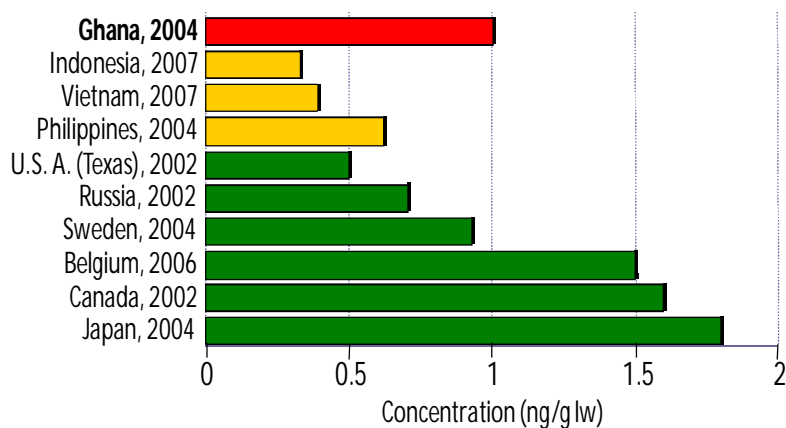


Figure 2. Comparison of mean level of HBCDs in the breast milk samples with other countries.

All the samples collected from the outskirts of the three cities; Accra, Kumasi and Tamale were pooled together (as rural) and compared with those collected in the three cities (as urban). Interestingly, the same congener pattern as observed when the three cities were treated separately was also evident which could point to similar exposure sources and buttresses the style of eating as stated earlier. In an attempt to know if there was any possible temporal variation, concentrations of PBDEs in Accra

were compared between 2004 and 2009 (Fig. 1). In 2004, total PBDEs varied between 0.61 and 7.3 ng/g lw (mean of 2.2 ng/g lw) while 2009 ranged from 1.30 to 9.08 ng/g lw (mean of 4.30 ng/g lw). Although there was no statistical difference between the two years, there seems to be an increase over the years but this statement is made with caution as not the same subjects were involved in both years. Although levels of HBCDs in the human breast milk collected in 2009 are yet to be quantified, levels of HBCDs in 2004 were lower than PBDEs in both 2004 and 2009. However, the mean HBCD level for 2004 was comparable to studies in Europe (Fig. 2) (Other data cited from Malarvannan et al. 2009). The presence of PBDEs and HBCDs in the human breast milk is particularly troubling due to exposure of nursing children.

Health risk assessment

Daily intakes of PBDEs by infants were calculated based on the assumption that the average breast milk consumption of a 5 kg infant was 700 g/day (Oostdam et al. 1999). The infant's daily intake of total PBDEs through milk in Ghana is below the reference dose for chronic oral exposure shown to cause various developmental effects in neonatal mice and rats (U.S. EPA 2008), implying minimal risk caused by PBDEs at present. Considering that there is no production of BFRs in Ghana, significant sources of BFRs could be electronic and electrical equipment or their wastes imported from developed countries such as USA and Europe. This is the first study to report on BFRs in human breast milk from Ghana.

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