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Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Cow Milk Samples from Ghana

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Abstract—Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are additive flame retardants widely used in plastics, furniture, textiles and electronics such as computers, DVDs and TV-sets. BFRs and polychlorinated biphenyls (PCBs) are lipophilic and have the propensity to bioaccumulate and biomagnify in food chains. In this study, concentrations of PBDEs, HBCDs and PCBs in 21 cow milk samples from Ghana were measured. PCBs and PBDEs were detected in all samples but not HBCDs. Levels of PCBs ranged from 2.1–45 ng/g lipid wt. in rural and 2.5–87 ng/g lipid wt. in urban samples. PBDE levels were 0.047–2.8 (rural) and 0.47–11 ng/g lipid wt. (urban). BDE-47 and BDE-99 were found in all samples with high proportion, whereas BDE-209 was detected in only 5 of the 21 samples but in high concentrations. Lack of correlation between concentrations of PCBs and PBDEs may suggest different exposure sources of PCBs and PBDEs. There is no production of BFRs and PCBs in Ghana and thus, significant sources/routes for PBDEs and PCBs could be dust-ingested food, and any electronic and electrical equipment or their wastes imported from developed countries, found at waste dumping sites where sometimes the cattle graze. This is the first study on BFRs in cow milk from Ghana.

Keywords: cow milk, PBDEs, PCBs, HBCDs, Ghana

INTRODUCTION

Brominated flame retardants (BFRs) constitute a diverse group of compounds mainly used to inhibit or minimize the extent of a fire. The representative additive flame retardants, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are widely used in plastics, paints, furniture, textiles, building materials and electronics such as computers, DVDs and TV-sets. As additive flame retardants, PBDEs and HBCDs are not chemically bound to the materials they protect. Due to the production processes, usage and disposal, they can be released from the products during their entire period of usage and disposal into the environment (Birnbaum and Staskal, 2004). The main sources of human exposure to PBDEs are through dust and food consumption (Darnerud *et al.*, 2001; Sjodin *et al.*, 2008). Previous studies have shown that food is a major route of human exposure for organochlorines such as PCBs and PCDD/Fs (Fuerst *et al.*, 1990; Duarte-Davidson and Jones, 1994). PBDEs are similar to PCBs in chemical structure. BFRs and PCBs are lipophilic, hydrophobic and have the propensity to bioaccumulate and biomagnify in biota (Sjodin *et al.*, 2003). Generally, fatty foods of animal origin are the major sources of human exposure to lipophilic contaminants (Fuerst *et al.*, 1990; Duarte-Davidson and Jones, 1994). Thus, consumption of milk and its products could contribute to the total dietary intake of these contaminants (Schaum *et al.*, 2003; Huwe and Smith, 2005; Pietrzak-Fiecko *et al.*, 2005; Durand *et al.*, 2008). In Ghana, with the introduction of Western-style dairy products, their consumption has grown. In spite of this, no information is so far available on the levels of persistent chemicals, especially BFRs and PCBs in milk and milk products of Ghana. The aim of the study was to explicate the contamination status of PBDEs, HBCDs and PCBs in cow milk from Ghana. This is the first study to report on BFRs in cow milk samples from Ghana.

MATERIALS AND METHODS

Sampling and study area

For this baseline study, raw cow milk samples were collected in March, 2009 from some kraals in Accra (the capital of Ghana) and the farm of the Council for Scientific and Industrial Research-Animal Research Institute (CSIR ARI) at Frafraha, also in the Greater Accra Region (urban), and Asutsuare in the Eastern Region of Ghana (rural). Accra is the largest city in Ghana in terms of industrial establishment and infrastructural development. It is a coastal city and one of the major e-wastes dumping sites in West Africa. On the other hand, Asutsuare is relatively a rural setting. All the samples were collected in glass bottles pre-cleaned at the Center for Marine Environmental Studies (CMES), Ehime University, Japan. The samples were not subjected to any chemical form of treatment. They were stored in cold boxes in the field and on returned to the laboratory in Accra kept in a deep freezer. The frozen samples were airlifted to CMES on dry ice and were kept in the Environmental Specimen Bank (*es*-BANK) of Ehime University at –25°C (Tanabe, 2006) until chemical analyses. Out of the samples, twenty-one from Accra (n = 13) and Asutsuare (n = 8) were used in analyzing for PCBs, PBDEs and HBCDs.

Analytical method

Briefly, about 50 g of cow milk sample was lyophilized and extracted with solvent extractor. Fat content was determined gravimetrically and fat was removed by gel permeation chromatography (GPC). The lipid removed extract was concentrated and loaded to silica gel column for clean up. Fourteen PBDE and

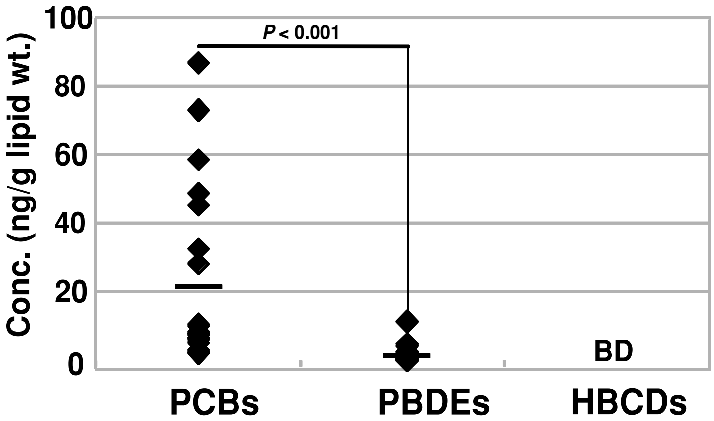

Fig. 1. Overall contamination status of PCBs, PBDEs and HBCDs. BD: below detection limit. Horizontal bars indicate mean values.

sixty-two PCB congeners were quantified using a gas chromatograph with mass spectrometer (GC-MS), while three HBCD isomers (α-, β-, γ-HBCD) were quantified using a liquid chromatograph coupled with a tandem mass spectrometer (LC-MS/MS) based on the method published elsewhere (Malarvannan *et al.*, 2009) with slight modification.

RESULTS AND DISCUSSION

PBDEs—Levels and distribution

PBDEs were detected in all the samples (Fig. 1). Total PBDE concentrations ranged between 0.47 and 11 ng/g lipid wt. in milk from the urban cows with a mean of 2.3 ng/g lipid wt. while the rural cows had a mean total PBDEs concentration of 1.0 ng/g lipid wt., varying from 0.047 to 2.8 ng/g lipid wt. In accordance with few data reported in the literature (Gruemping *et al.*, 2006), BDE-47 and -99 were found in all cow milk samples. BDE-47 on average contributed to over 50% of the total sum of the Mono- to Deca-BDEs. For the rural samples, the exact value was 55% and for the urban samples the contribution of BDE-47 was 48% (Fig. 2). The average contribution of BDE-99 to total PBDEs was 18% each for the rural and urban samples. It appears that BDE-47 and BDE-99 are the main contributors to PBDE contamination in food. From Fig. 2, it could be suggested that PBDE commercial mixtures; Penta-BDE and Deca-BDE, have been used in Ghana and or BDE-47 and BDE-99 have higher bioavailability and persistence than the higher brominated congeners.

An important human exposure pathway for PCBs is via atmospheric deposition in plants and uptake in grazing animals with consequent contamination of meat and dairy products (McLachlan, 1996). The same exposure pathway may also be

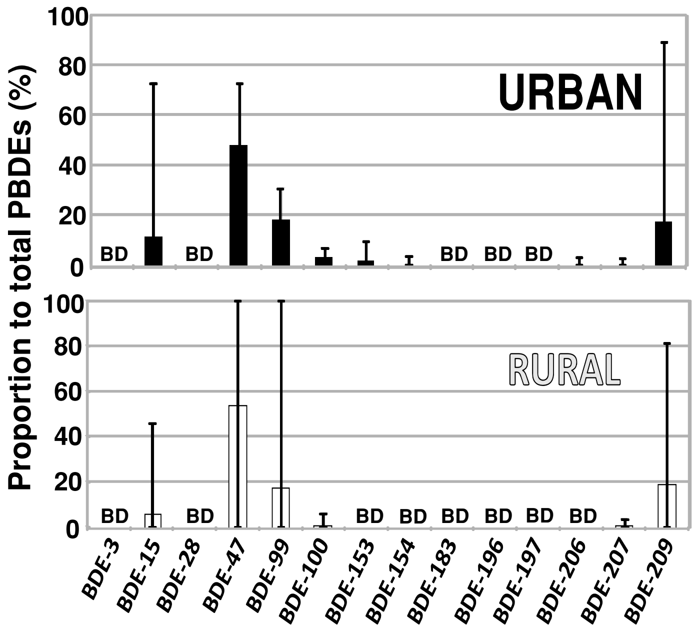

Fig. 2. Congener profile of PBDEs in urban and rural samples. BD means below detection limit.

expected for PBDEs. BDE-209 was found in relatively high concentrations in 5 of the 21 samples, ranging from 2.0 to 10 ng/g lipid wt. This could be due to its specific binding to lipoproteins (Huwe *et al.*, 2008). Due to its hydrophobicity and low vapour pressure, BDE-209 binds to fine particles which can undergo long-range transport as seen in deposition samples from the Central Baltic Proper (Ter Schure *et al.*, 2004). Reference soil samples from a Swedish study (Sellstrom *et al.*, 2005) and grizzly bears feeding on terrestrial food (Kierkegaard *et al.*, 2007) also showed the presence of BDE-209. BDE-15 was detected in 5 of the 13 urban cow milk samples (0.18–0.53 ng/g lipid wt.) and in 2 of the 8 rural milk samples (0.16 and 0.27 ng/g lipid wt.). Furthermore, few urban samples contained BDE-153, -154 and -206 in small concentrations, while these were not detected in any of the rural samples. BDE-3, -28, -183, -196 and -197 were not detectable in any of the analyzed milk samples from either area in this study. The average lipid content was 4.5% in this study, varying between 0.9 and 7.4%. A plot of total PBDE levels (ng/g wet wt.) against lipid content (%) gave a correlation (r) of 0.867, $p < 0.001$ (figure not shown), which could imply that the higher the fat content, the higher the PBDE level. HBCDs levels were below the detection limit in all the samples.

PCBs—Levels and distribution

Like PBDEs, PCBs were detected in all the samples, and significant difference

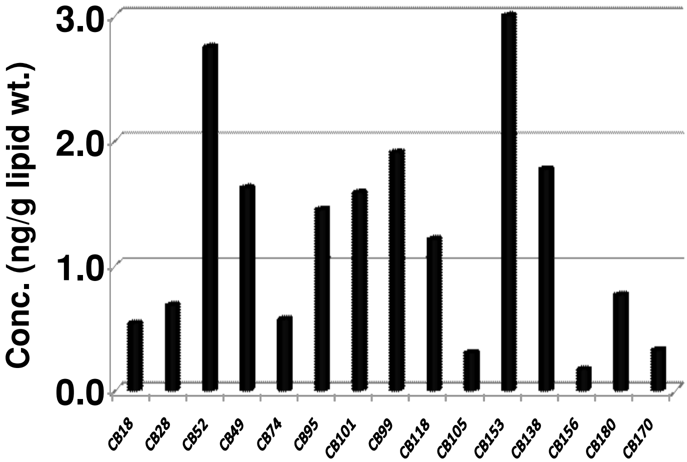

Fig. 3. Overall congener profile of PCBs in this study.

($p < 0.001$) was observed between PCB and PBDE concentrations (Fig. 1). Total PCB concentrations (sum of 62 congeners) of the urban samples varied from 2.5–87 ng/g lipid wt. with a mean ∑PCBs concentration of 27 ng/g lipid wt. while the rural samples had a mean ∑PCB level of 14 ng/g lipid wt., ranging from 2.1–45 ng/g lipid wt. The order of homologues was: Hexa > Penta > Hepta > Tetra. The overall dominating congener pattern was: CB-153 > CB-52 > CB-99 > CB-138 > CB-49 > CB-101 (Fig. 3) and contributed 14%, 13%, 9%, 8%, 7.4% and 7.2%, respectively to the total PCBs load. A side note to this study was that although there was a statistical difference between levels of PCBs and PBDEs ($p < 0.001$) in the cow milk samples, correlation between PCBs and PBDEs was not significant (figure not shown), possibly, indicating different exposure sources.

The presence of congeners CB-153, CB-138, CB-118 and CB-180 in the milk samples from Ghana is a cause for concern as they are persistent. These congeners are typically substituted at both para positions (4,4′) and according to McLachlan (1993), the 4,4′ substitution is the key to PCB persistence in cows because the formation of the intermediate arene oxide at the 4-position is inhibited.

By consuming large masses of herbage or silage, dairy cows transfer PCBs and other persistent semi-volatile organic contaminants into the human food chain. Some compounds are transferred effectively unchanged from grass to milk and dairy products (e.g. PCBs 138, 153, 180), with the cow acting as an efficient "conduit" to humans (Thomas *et al.*, 1999).

Comparison of PBDEs and PCBs with other studies

Compared with few available data on cow milk, which measured levels up to Octa-BDE, the mean total PBDE concentration from this study (0.78 ng/g lipid wt. excluding BDE-209) exceeded mean levels found in Spain (0.63 ng/g lipid wt.) (Bocio *et al.*, 2003); Ireland (0.40 ng/g lipid wt.) and Switzerland (0.20 ng/g lipid wt.) (Gruemping *et al.*, 2006). Total PCBs from this study also exceeded levels reported for Slovenia (Cerkvenik *et al.*, 2000); UK (Sewart and Jones, 1996) and Siberia (Mamontova *et al.*, 2007) but was lower than a Polish study (Pietrzak-Fiecko *et al.*, 2005).

Factors controlling variability in milk concentrations

The differences in concentrations measured in this study are likely to be influenced by feeding and lactation patterns, soil ingestion and the bioavailability of soil-ingested PCBs and PBDEs, and proximity to contemporary deposition sources which will increase concentrations in vegetation. Although a complex pattern of accumulation caused by these factors should be considered, at least, it could be said that significant sources of PBDEs and PCBs do exist even in developing countries like Ghana. The free-range option of feeding adopted by most Ghanaian cattle farmers, although city authorities frown upon this practice, could be the major source of these contaminants in the cows' milk. These cattle roam freely on grasslands and sometimes on waste dumping sites which contain some discarded electronic appliances. There is no production of BFRs and PCBs in Ghana, and thus, potential source of PBDEs and PCBs in the cows' milk could be dust-ingested food, and any electronic and electrical equipment or their wastes from developed countries such as USA and Europe, found on waste dumping sites where sometimes the cattle graze.

CONCLUSIONS

PCBs and PBDEs were detected in all samples but not HBCDs. Statistical difference was observed between concentrations of PCBs and PBDEs (all samples together), but between urban and rural, there was no significant difference in levels of PCBs and PBDEs although urban samples had relatively high concentrations. BDE-47 and BDE-99 were found in all the samples with high proportion, whereas BDE-209 was detected in only 5 of the 21 samples but in high concentrations. The detection of BDE-47, BDE-99 and CB-153, CB-138 in the milk samples is a cause for concern due to their persistence and bioavailability.

Comparison with other studies indicates that PBDEs and PCBs in cows' milk from Ghana were relatively high. Lack of correlation between concentrations of PCBs and PBDEs may suggest different exposure sources of PCBs and PBDEs. Considering that there is no production of BFRs and PCBs in Ghana, significant sources of PBDEs as well as PCBs in the cows' milk could be from dust-ingested food, and any electronic and electrical equipment or their wastes imported from developed countries such as USA and Europe, which sometimes are found at the dumping sites where the cattle graze.

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