

ASSESSMENT OF HUMAN EXPOSURE TO PCBs AND BFRs THROUGH FISH CONSUMPTION IN GHANA

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Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are representative brominated flame retardants (BFRs) used in different kinds of plastics, electrical and electronic equipment, and textiles as non-covalent additives¹. These compounds can leak out into the environment during the entire life cycle of the products, including final waste disposal. Polychlorinated biphenyls (PCBs) are a group of synthetic chlorinated biphenyls. Owing to their non flammable and insulating properties, they have been used widely as coolants and lubricants in transformers, capacitors and other electrical equipment. The widespread occurrence of these contaminants in the environment deserves growing concern because of their stability, lipophilicity and potential toxicity. Some investigations have confirmed that more than 90% of human contaminants come from food². Risk assessment of persistent organic pollutants (POPs) in food for human is therefore of paramount importance. Although fish products account for only about 10% of diet^{3,4}, it is one of the main sources of chemical contaminants which may be detrimental to human health. In Ghana, fish is recognized as the most important source of animal protein^{5,6}. Estimates suggest that over 60% of animal protein in the Ghanaian diet comes from fish and the average per capita fish consumption is estimated at 20-25kg/year, close to 10kg higher than the world average of 16kg⁶. However, there is not sufficient information on residual levels of PCBs and no information on BFRs in food including fish from water bodies in Ghana. Thus, it is very timely to start research on POPs in fish from representative water bodies. This is the first study to report BFRs in fish samples from Ghana, and arguably from Africa.

Materials and methods

Ghana is located on the west coast of Africa with a population of about 25 million. Tilapia fish samples were collected in August 2010 from three water bodies; Lake Volta and Weija Lake (two important freshwater bodies in Ghana), Benya lagoon and an aquaculture pond (ARDEC). 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 until extraction and chemical analyses. Twenty-two samples, made up of specimens from Weija Lake (*n*=7), Volta Lake (*n*=6), Benya lagoon (*n*=5) and ARDEC (*n*=4) were used in analyzing for PBDEs, HBCDs and PCBs. Briefly, approximately 30g of fish sample was lyophilized and extracted with accelerated solvent extractor (ASE 100, Mitsubishi). 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. Forty-two PBDE congeners and sixty-two PCB congeners were quantified using gas chromatograph with mass spectrometry (GC-MS) while three HBCD isomers (α -, β -, γ -HBCD) were quantified using liquid chromatograph with tandem mass spectrometry detector (LC-MS-MS), based on the methods published elsewhere⁷. Procedural blanks were analyzed simultaneously with each batch of samples to check for interference or contamination from solvents and glass wares.

Results and discussion

PCBs – Levels, distribution and profile

Among the contaminants, PCBs were significantly higher than PBDEs and HBCDs (Fig. 1) probably due to high consumption in the past and/or higher bioaccumulation properties of PCBs. PCBs were detected in all fish samples of the present study with varying concentrations among species and locations. Concentrations of total PCBs (sum of 62 congeners) in all the samples varied between 1.1 and 300 ng/g lipid weight (ng/g lw) with a mean of 55 ng/g lw.

The most predominant congeners in the fish samples were PCB 138, 153 and 180 (Fig. 2). In Ghana, plasticizers, certain paints, fire retardants and lubricants constitute the largest source of PCBs releases⁸. There is no production of PCBs in Ghana but the results indicate a notable contamination by PCBs which may be associated with anthropogenic activities. The higher relative concentration of the more volatile and less lipophilic lower-chlorinated congeners such as CB-28, -52 and -99 in the samples could be due to these PCBs being redistributed through air and air borne particles as Ghana is prone to the yearly effect of the Harmattan wind which picks up fine dust particles from the Sahara desert⁷. The source of PCBs in the Sahara desert could be atmospheric deposition from Europe and off the West African coast. There are major emissions of PCBs and different source types including ships' graveyard in parts of West Africa than accounted for in current global atmospheric emission estimates⁹.

To understand the magnitude of contamination, the mean concentration of total PCBs in fish from Ghana was compared with those reported in different fish studies in other countries. Mean level of PCBs (55 ng/g lw) from this study was higher than previous studies in Cambodia, Taiwan and Thailand and comparable to Hong Kong but lower than in Indonesia, Turkey, Sweden and North America. Global comparison of PCBs confirms that developed countries were more contaminated by PCBs than developing nations although comparison between results is sometimes difficult, because of the variability of PCB congeners that have been analyzed in the different surveys and differences concerning the expression of the results (wet weight or lipid weight).

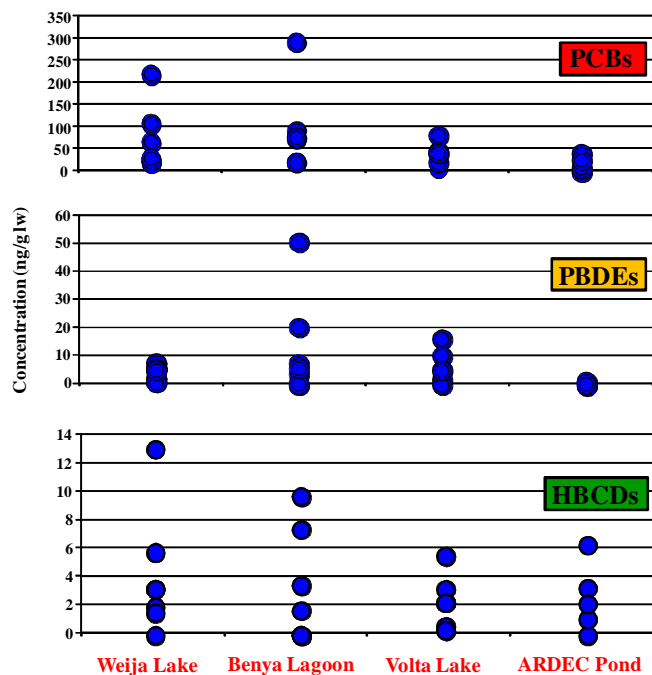


Fig. 1. Contamination status of PCBs and BFRs in fish from Ghana.

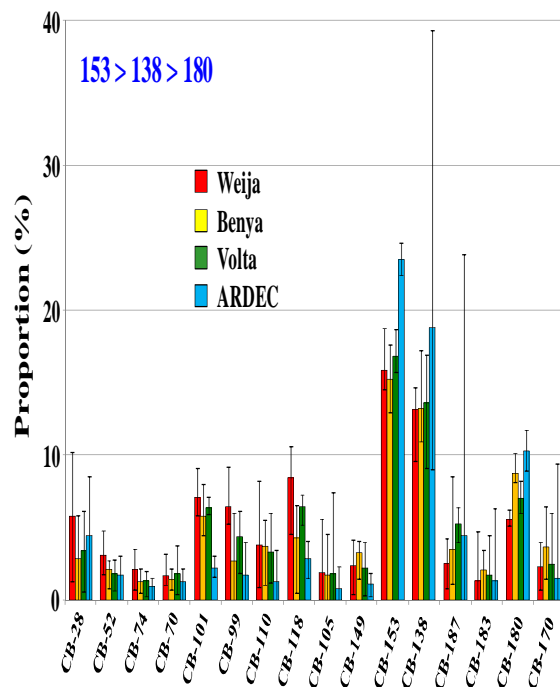


Fig. 2. Congener profile of PCBs in fish from Ghana.

PBDEs – Levels, distribution and profile

Concentrations of PBDEs ranged from 0.01 to 52 ng/g lw (mean of 6.7 ng/g lw). Among the PBDEs, BDE-47 was the predominant congener with an average contribution of 37.5% in the samples. Because BDE-47 is a major constituent of the Penta-BDE technical mixtures, its preferential accumulation in fish from Ghana may indicate that these technical mixtures have been used in Ghana. The dominance of BDE-47 in the present study was consistent with the general pattern found in biota samples in other studies^{10,11}. Metabolic differences, age of the fish, and lipid content as well as other physiological differences among fish species are also possible reasons for the observed PBDE patterns¹². Land runoff compared with other means of deposition may be considered as one of the most

important pathways for PBDEs entering into water bodies. Besides, the Benya lagoon has more intensive trawling (shipping) activities than the other water bodies in this study, due to its proximity and opening into the sea which is also a potential source for PBDEs¹³. The detection of BDE-209 in some fish samples of the present study may suggest the usage of Deca commercial mixtures in Ghana or deca-BDE sources existed in Ghana. Because of the higher molecular weight and larger octanol/water partition coefficient ($\log K_{ow} \sim 10$) of BDE-209, it has lower bioavailability compared to other PBDE congeners. However, debromination of BDE-209 to more bioavailable metabolites has been found to occur in fish tissues¹⁴. Moreover, many studies have concluded that BDE-209 was bioavailable and could undergo metabolic debromination¹⁵. BDE-49 was found in some fish with levels many times lower than BDE-47 and similar to the profiles reported by Hites et al.¹⁰ in both wild and farmed salmon, and by Covaci et al.¹⁶ in mussels, eel and carp. BDE-66 was also found in few fish samples in our study as is often reported in other studies^{10,17}. Comparison with other studies indicates that the PBDEs levels in the present study were in the low or medium among the levels around the world. However, the increasing textiles, chemical and electronic waste activities in Ghana may bring more PBDEs contamination. Moreover, various environmental and biological processes of PBDEs in the Ghanaian environment are still unknown. Hence, more studies on PBDEs should be conducted in order to understand the risks they may pose to humans in Ghana via fish consumption/dust inhalation.

HBCDs – Levels and distribution

HBCDs were detected in some of the fish samples from the present study. Mean concentrations were: Weija lake (4.0 ng/g lw), Benya lagoon (3.1 ng/g lw), Volta lake at Akosombo (2.2 ng/g lw) and ARDEC (2.5 ng/g lw). Variations in concentrations could partially be due to their bioaccumulation, frequency and extent of HBCDs exposure. The largest release of HBCDs is estimated to be contaminated water from production of insulation boards, water and air from textile coating and diffuse release during the life cycle of insulation boards and textiles¹⁸. Judging from this, the small-scale textile industries dotted across Ghana could be a potential source of exposure. The presence of a textile industry at Akosombo could be a major source of HBCDs in fishes from the Volta Lake and ARDEC pond. Among the HBCDs, α -HBCD was found to be the predominant isomer in the fish species, followed by γ - and β -HBCDs. Previous studies have also found that α -HBCD was the major diastereoisomer of HBCDs in many of organisms including fish, birds and marine mammals¹⁹. These results indicate that α -HBCD can be selectively accumulated in organisms. One explanation may be that γ -HBCD can be metabolized more quickly than α -HBCD in organisms²⁰; others include a preferential uptake of α -HBCD, possibly due to a higher water solubility of α -HBCD (48.8 $\mu\text{g/L}$) than β - (14.7 $\mu\text{g/L}$) or γ -HBCDs (2.1 $\mu\text{g/L}$)²¹. The levels of HBCDs in fishes from the present study were higher than previous studies in the Philippines and Indonesia but lower than in Sweden, the Netherlands, Norway, China, Canada and USA. Higher levels of HBCDs as compared to other regions have been reported in various environmental matrices in Europe²² where HBCDs are heavily used, due to higher demand of this particular BFR. Available estimates of world market demand for HBCDs (around 17 kilotons) indicate that 57% and 23% were consumed in Europe and Asia, respectively in 2001²³.

Estimated daily intakes via fish consumption

An estimation of the dietary exposure of the Ghanaian population to the contaminants through fish consumption was evaluated. Using the data acquired from the present study (on wet weight basis), estimated daily intakes (EDIs) of PCBs, PBDEs and HBCDs via fish consumption were calculated by multiplying per capita fish consumption values with the contaminants residual levels, expressed as ng/kg/body weight/day assuming a typical body weight of 60 kg. The average per capita fish consumption value in Ghana is about 25 kg. The estimated dietary exposure levels of the contaminants in the present study were

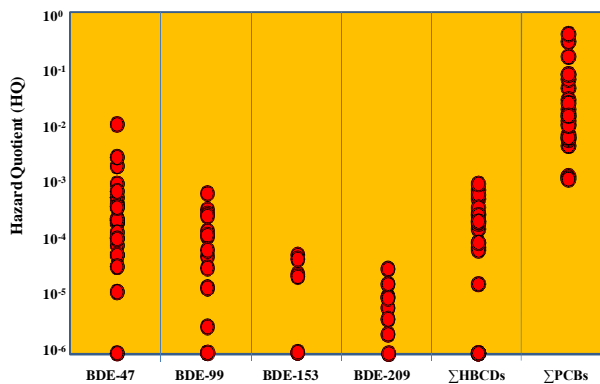


Fig. 3. Daily intakes of PCBs and BFRs via fish consumption in Ghana.

below the threshold value of 1, indicating less potential health risk of these contaminants to Ghanaians via fish consumption (Fig. 3). In comparison with other reported studies, our findings indicate a moderate contamination level; however, continuous study of the temporal trends of PCBs and BFRs in Ghana is needed to evaluate possible long-term impacts to human health via fish consumption since fish is recognized as the most important source of animal protein in Ghana.

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