

# ASSESSMENT OF HUMAN EXPOSURE TO HALOGENATED COMPOUNDS AND ELECTRONIC WASTE RECYCLING ACTIVITIES IN GHANA

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## Introduction

Humans in their daily lives are exposed to a cocktail of chemicals including the legacy and emerging persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs). Contamination by POPs has received increasing attention internationally. In 2001, the Stockholm Convention on POPs was established as a global treaty to protect human health and the environment from these chemicals. These POPs tend to persist in the environment for a long period of time, become distributed globally, accumulate in the lipids of humans and wildlife, and bind to sediments<sup>1</sup>. In the 21<sup>st</sup> century, electronic waste (e-waste) recycling has emerged as a critical global environmental and human health issue. Ghana is a major destination for e-waste in Africa. At Agbogbloshie in Ghana's capital city, Accra is the location of the major e-waste dumping site in Ghana. Most of the e-waste comes from Europe and North America. In 2005, Ghana ratified the UN's Basel Convention on the transboundary movements of hazardous wastes and their disposal, but its provisions are yet to be incorporated into a national legislation and so the dangers posed to humans and the environment in Ghana from such e-waste activities are not properly addressed. E-waste contains harmful chemicals such as BFRs and classical toxic trace elements (TEs) such as Pb, Cd, Hg, As and Cr, as well as rare TE including Sb, In and Tl. Due to the crude recycling techniques used, large quantities of POPs and toxic TE are released into the environment and eventually reach humans<sup>2</sup>. Polychlorinated biphenyls and BFRs such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) were measured in human breast milk and fish samples collected from Ghana to elucidate the contamination status and assess the health risk associated with the intake of these contaminants.

## Materials and methods

Human milk samples ( $n=42$ ) were collected from primiparous mothers in 2009 from three locations in Ghana: Accra (coastal) ( $n=16$ ); Kumasi (forest zone) ( $n=14$ ) and Tamale (savannah) ( $n=12$ ). In each city, samples were taken from both urban and rural areas. Twenty five samples collected from Accra in 2004 were also analyzed in this study to assess the temporal variation. Forty tilapia fish samples were obtained in August 2010 from: Weija Lake ( $n=10$ ), Volta Lake (Akosombo) ( $n=6$ ), Volta Lake (Sogakope) ( $n=4$ ), Benya lagoon ( $n=8$ ), Keta lagoon ( $n=6$ ) and an aquaculture pond (ARDEC) ( $n=6$ ). 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  $-25^{\circ}\text{C}$  until chemical analyses. Forty-two PBDE congeners and sixty-two PCB congeners were quantified using gas chromatograph with mass spectrometry (GC-MS) while three HBCD isomers ( $\alpha$ -,  $\beta$ -,  $\gamma$ -HBCD) were quantified using liquid chromatograph with tandem mass spectrometry detector (LC-MS-MS), based on the methods used and described in our previous works<sup>3,4,5</sup>. Procedural blanks were analyzed alongside with the samples.

## Results and discussion

### *PCBs, PBDEs and HBCDs in Human Breast Milk and Fish Samples*

PCBs, PBDEs and HBCDs were detected in all the analyzed matrices from Ghana. Mean concentrations in human breast milk were 62 ng/g lw for PCBs, 4.5 ng/g lw for PBDEs and 0.54 ng/g lw for HBCDs. Nursing mothers from Accra had the highest contaminants levels. Statistical differences were found between Accra and Tamale, and Kumasi and Tamale indicating that nursing mothers from Accra and Kumasi are more exposed. This could be due to the significant sources such as the location of the biggest e-waste site in Accra and differences in food preference among the locations. In order to assess the magnitude of contamination, human milk results from this study were

juxtaposed with some other studies. Albeit Ghana is a non-industrialized country compared to Europe, North America and some Asian countries, the assessment showed higher levels of PCBs, PBDEs and HBCDs in Ghana than many Asian countries, almost similar to Europe but lower than in North America. Significant ( $p < 0.001$ ) increases were found in the concentrations of PCBs and PBDEs in the human breast milk samples collected in 2009 than those in 2004 showing that PCBs and PBDEs increased in the Ghanaian environment within the 5-year period. The fish concentrations were: PCBs (1.1 - 300 ng/g lw; mean, 62); PBDEs (<0.01 - 52 ng/g lw; mean, 7.3) and HBCDs (<0.01 - 8.5 ng/g lw; mean, 1.2). Benya lagoon was the most contaminated water body followed by the Weija Lake, resulting from the discharge of untreated domestic wastewater and industrial effluents. Generally, CB-153, -138, -180; BDE-47 and  $\alpha$ -HBCD were the dominant contributors in the human milk and fish samples. The detection of BDE-47 and BDE-209 in the sample matrices (Fig. 1) as in cow milk samples<sup>6</sup>, suggests that penta- and deca-BDE technical mixtures have been used or sources of these mixtures exist in Ghana. In comparison with other reported fish studies, our findings on fish indicated a moderate contamination level; however, continuous study of the 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.

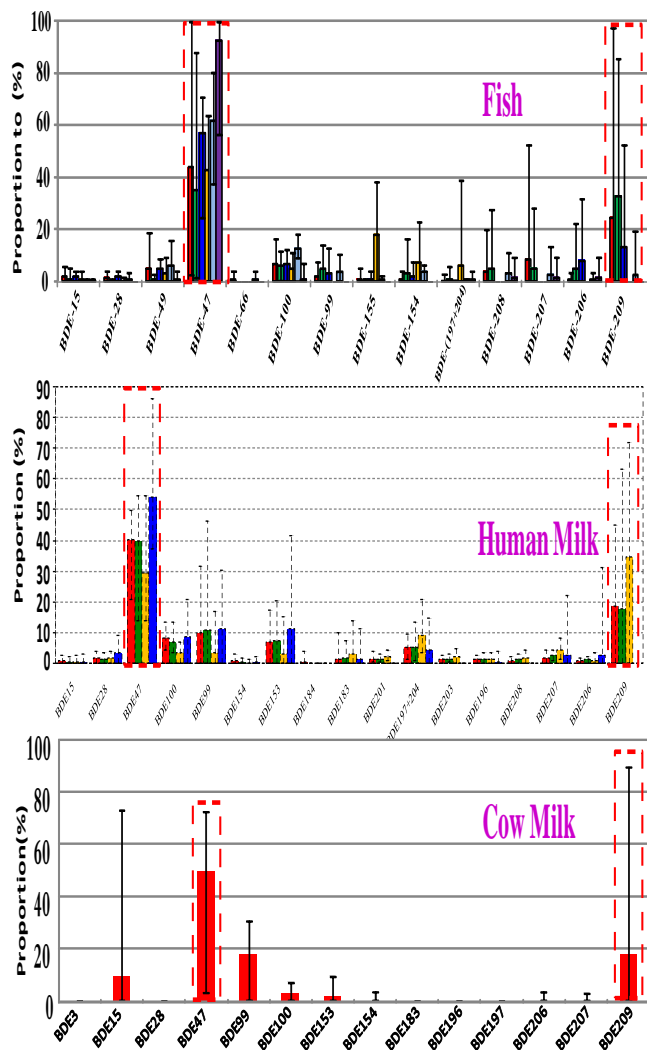


Fig.1. Congener profile of PBDEs in sample matrices from Ghana.

#### Estimated daily intakes via human milk and fish consumption and toxicological risk assessment

Hazard quotient (HQ) values [calculated as the ratio of the estimated daily intake (EDI) of the target contaminant to the reference dose] *via* human milk showed that all the PCBs exceeded the threshold of 1 (Fig. 2), indicating potential health risk for the newborns. An assessment of the dietary exposure of the Ghanaian populace to the contaminants through fish consumption was carried out. Using the data acquired from the present study (on wet weight basis), EDIs of PCBs, PBDEs and HBCDs *via* fish consumption were calculated by multiplying the daily fish consumption value by the residual levels of the contaminants, expressed as ng/kg bodyweight/day assuming an average body weight of 60 kg for Ghanaians. With the mean consumption of fish and seafood in Ghana as 78 g/day<sup>7</sup>, the EDIs of BDE-47, BDE-99, BDE-153, BDE-209,  $\Sigma$ HBCDs and  $\Sigma$ PCBs in the present study were below the reference doses (RfDs) for chronic oral exposure values (Fig. 3), suggesting that fish consumption is unlikely to be a source to human health with regard to uptake of PCBs, PBDEs and HBCDs. However, since some EDIs of PCBs (*via* fish) were close to the RfD, further studies are warranted as PCBs are known carcinogens and the consumption of fish is the primary route of human exposure. In Ghana, there is no legislation regarding PCBs and BFRs maximum allowed concentration specifically in fish. Toxicological risk related to PCBs was assessed through the comparison of measured concentrations with the legal limits of 2000 ng/g fresh weight, proposed by the Food and Drug Administration, USA<sup>8</sup> for human consumption of fish products, and

the maximum value of 100 ng/g fresh weight for the sum of the seven indicator PCB congeners in fish proposed by the European Commission (EC) draft regulation<sup>9</sup>. Concentrations of PCBs measured in all the specimens in our study were below these food safety guidelines.

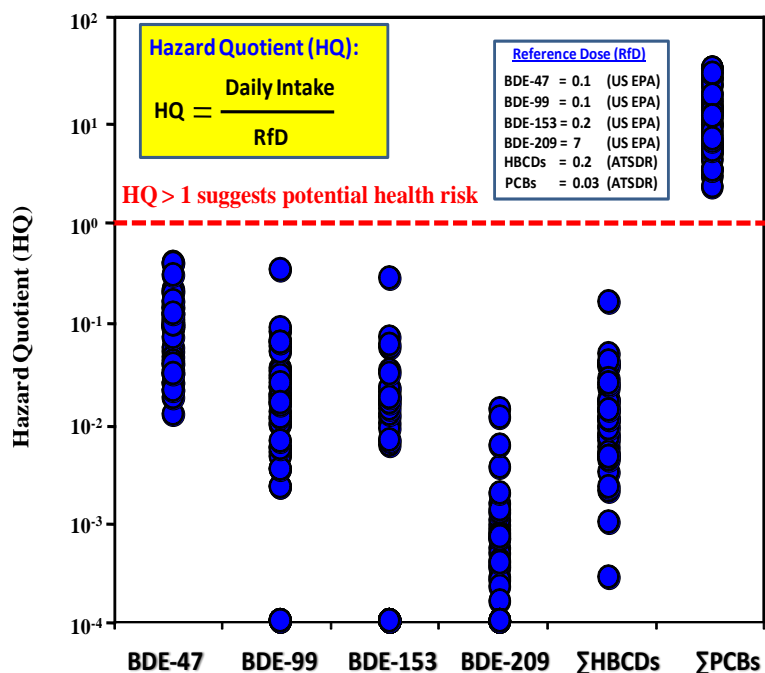


Fig. 2. Estimated hazard quotient values for BDE-47, BDE-99, BDE-153, ΣHBCDs and ΣPCBs via human breast milk in Ghana.

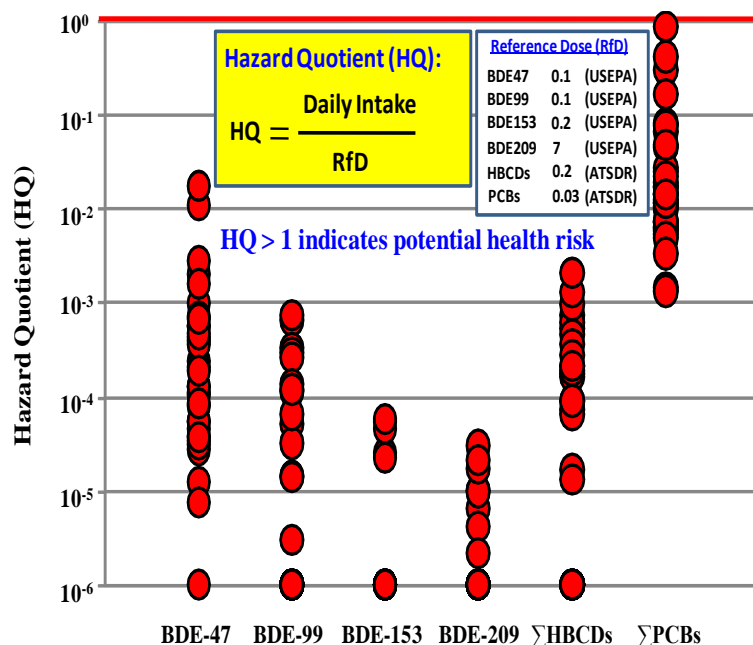


Fig. 3. Estimated hazard quotient values for BDE-47, BDE-99, BDE-153, ΣHBCDs and ΣPCBs via fish consumption in Ghana.

#### Association between target contaminants and lipid content (%)

A positive albeit weak correlation ( $r^2=0.293$ ) between PCB concentrations (wet weight) and lipid content was found. Similarly, a positive but weak correlation ( $r^2=0.212$ ) between concentrations of PBDEs and lipid content was established. Regression analysis indicated that the capacity to accumulate HBCD was not correlated to lipid content for the species studied. Concentrations of PBDEs correlated with those of PCBs in all fish ( $r^2=0.613$ ,  $p<0.001$ ) (Fig. 4) implying that PBDEs are as prevalent as PCBs in the studied areas with similar sources and/or that the two contaminants may have similar environmental behaviour. Both HBCDs and PBDEs have been used as flame retardants. Despite this, there was no clear relationship between both pollutants as the weak correlation coefficient ( $r^2=0.20$ ) revealed. The lack of correlation between HBCDs and PBDEs or PCBs suggests different exposure sources. Textile manufacturing is a significant source of HBCDs in the environment while e-waste is the major source of PBDEs and to some extent PCBs.

#### Conclusions

PCB-153, -138, -180; BDE-47 and α-HBCD were the major contributors in the human milk and fish samples. The accumulation of BDE-47 and the detection of BDE-209 may suggest that Penta- and Deca-BDE technical mixtures have been used in Ghana. Estimated hazard quotient (HQ) values for all the PCBs via human milk exceeded the threshold of 1. However, the HQ values through fish were less than 1. PCBs in dirty oils and obsolete equipment could be potential sources in Ghana. Significantly higher levels of PCBs and PBDEs in human milk were found in 2009 than in 2004. The increasing trend of PBDEs in human milk in Accra indicates that the increase in WEEE import and primitive recycling have increased the levels of PBDEs

in the average population of Accra. Similarly, significantly higher levels of iron, lead and antimony were found in urine of e-waste recycling workers in Accra than those of a reference population from Obuasi, situated at a distance of 200 km northwest of Accra<sup>10</sup>. The high levels of antimony, used as flame retardant synergist of BFRs, in urine of e-waste workers indicate critical exposure to antimony and therefore most likely also, BFRs in the workers. There is therefore an urgent need to assess BFRs and heavy metals exposure to the e-waste workers and the population in the vicinity of the e-waste recycling site. The government of Ghana as a matter of urgency must curtail the dumping of e-waste in the country and associated recycling activities by passing a legislation to forestall a looming catastrophe. Health is not wealth but environmental health is environmental wealth.

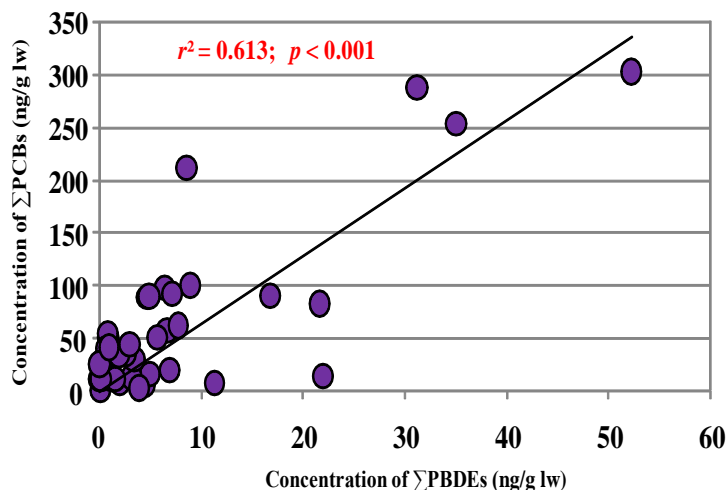


Fig.4. Relationship between ΣPCBs and ΣPBDEs in fish from Ghana.

#### Acknowledgments

For their assistance during the sampling campaign, we thank Mrs. Gifty Afua Asante, Mr. Henry Asabore Boham and staff of the CSIR Water Research Institute, especially Mr. Samuel O. Agyei (driver), Drs. Joseph K. Ofori, Felix Y. K. Attipoe, Yaw Opoku-Ankomah and the late Dr. Stephen Dapaah-Siakwan. We also acknowledge Dr. Jiro Ogawa, Environmental Specimen Bank (es-BANK), CMES, Ehime University, Japan for sample management. This study was supported by the Global COE Program from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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