DIOXIN-LIKE POLYCHLORINATED BIPHENYLS, POLYCHLORINATED DIBENZO-*p*-DIOXINS AND POLYCHLORINATED DIBENZO FURANS IN EDIBLE FISH FROM FRESH WATER BODIES IN GHANA

Adu-Kumi S[1,2], Kawano M[3], Shiki Y[3]

[1]Chemicals Control and Management Centre, Environmental Protection Agency, P. O. Box MB 326, Accra, Ghana. [2]Department of Nuclear and Environmental Protection, Graduate School of Nuclear and Allied Sciences, University of Ghana, Legon, Accra, Ghana. [3]Department of Environment Conservation, Ehime University, 3-5-7 Tarumi, Matsuyama, 790-8566 Ehime, Japan.

Introduction

Diet and food consumption constitute an important pathways of human exposure to Persistent organic pollutants (POPs) and ingestion represents the main route of exposure for POPs for the general population compared to other exposure routes such as inhalation and dermal contact[1]. Risk assessment of POPs in food for human health is therefore of paramount importance. Although fish products account for only about 10% of diet[2] 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[3]. PCBs and PCDDs/Fs in food including edible fish from freshwater bodies in Ghana to ascertain such assumption. Lake Volta, Lake Bosumtwi and the Weija Lake, are three important freshwater bodies in Ghana. Large populations in the urban and rural communities depend on the three water bodies for their livelihoods and consume large amounts of fish, especially redbelly tilapia (*Tilapia zillii*) and catfish (*Clarias spp*., *Heterobranchus spp*.), which abound in these waters. These species are farmed in the water bodies as food[4]. Thus it is of utmost importance to investigate the status of POPs in fish from these representative water bodies. The present study provides information on the residue levels of dl-PCBs and PCDD/Fs in edible fish from Lake Volta, Lake Bosumtwi and Weija Lake and discusses their potential for health risks to the general population of Ghana.

Materials and Methods

Two species of fish samples (redbelly tilapia and catfish) were randomly collected from three locations in Ghana, namely, Lake Volta, Lake Bosumtwi and the Weija Lake in September 2008. Catfish from Lake Volta was however purchased from a local market at Madina, a suburb of Accra, the capital of Ghana. Fish samples were wrapped in aluminium foil, placed in polyethylene bags, stored under ice and transported to Japan where they were stored frozen at -20 °C until they were subjected to chemical analyses. The objectives of the sampling strategy were, among other things, using fish as a bio-indicator: (a) to conduct an exploratory investigation in obtaining preliminary information on the occurrence of dl-PCBs and PCDD/Fs in biota from the three major water bodies in Ghana; and (b) to benchmark the three water bodies so that levels of dl-PCBs and PCDD/Fs in biota can be compared over time. Approximately 40 g of edible portions of all fish samples (n = 13) were separately homogenized with anhydrous sodium sulphate, and subsequently extracted in Soxhlet apparatus with dichloromethane. Each extract was then concentrated and an aliquot of the extract dissolved in hexane. Prior to clean-up, each extract was spiked with known amounts of ^{13}C-labeled surrogates (Wellington Laboratories, Guelph, ON, Canada) for all 2,3,7,8-substituted PCDD/Fs congeners and all dl-PCBs as internal standards for the validation of the clean-up procedure. Each of the spiked solutions was then treated with concentrated sulphuric acid (H_2SO_4). The H_2SO_4 clean-up step was repeated until the H_2SO_4 fraction remained clear. The hexane layer was separated and washed with water. Each solution was purified (eluted) on multi-layer columns, containing sodium sulphate (2 g), 10% (w/w) silver nitrate-silica (2 g), silica gel (2 g), 22% (w/w) potassium hydroxide-silica gel (0.5 g), with hexane (100ml). Each eluate was concentrated eluted with 10% dichloromethane in hexane and toluene on an activated carbon/silica gel column to obtain mono-*ortho* PCBs, non-*ortho* PCBs, and PCDD/F congeners. All measurements were taken at the Department of Environment Conservation, Ehime University, 3-5-7 Tarumi, Matsuyama, 790-8566 Ehime, Japan. The purified sample solutions were analyzed by HRGC/HRMS (JMS-700D and JMS-800D, JEOL Ltd., Kokyo, Japan) equipped with DB-5ms capillary column (60 m length, 0.25 mm i.d. and 0.25 micrometer film thickness, J & W Scientific, USA).

Results and Discussion

Chemical analyses were carried out on all samples (n = 13) as indicated in section 3.2. Statistical analysis (*t*-test) showed that the differences in concentrations of the various analytes in fishes of the same species from the same locations were insignificant ($p > 0.05$). Average concentrations of measured analytes in the same species are therefore reported in this study. The concentration (ngg^{-1} lipid wt. and pgg^{-1} lipid wt.) data (average, minimum and maximum) of all analytes in tilapia and catfish from the three freshwater bodies under investigation are as shown in Table 1.

Table 1: Average concentrations of PCDD/Fs and dl-PCBs (pgg^{-1} lipid wt.) in fish from Lake Volta, Lake Bosumtwi and Weija Lake

Compound	Average concentrations (pgg^{-1} lipid wt.)	Tilapia = 9		Catfish = 4	
		Max	Min	Max	Min
2,3,7,8,-TCDD	0.65	1.70	0.49	0.28	0.18
1,2,3,7,8,-PeCDD	0.32	<LOD	<LOD	0.32	<LOD
1,2,3,4,7,8-HxCDD	2.60	2.60	<LOD	<LOD	<LOD
1,2,3,6,7,8-HxCDD	2.70	2.70	<LOD	<LOD	<LOD
1,2,3,7,8,9-HxCDD	5.00	5.00	<LOD	<LOD	<LOD
1,2,3,4,6,7,8-HpCDD	1.00	1.40	0.93	0.72	<LOD
OCDD	2.60	4.30	<LOD	1.80	<LOD
2,3,7,8-TCDF	3.30	4.20	2.40	1.70	4.30
1,2,3,7,8-PeCDF	2.50	2.50	<LOD	<LOD	<LOD
2,3,4,7,8-PeCDF	0.93	<LOD	<LOD	0.93	<LOD
1,2,3,4,7,8-HxCDF	<LOD	<LOD	<LOD	<LOD	<LOD
1,2,3,6,7,8-HxCDF	<LOD	<LOD	<LOD	<LOD	<LOD
1,2,3,7,8,9-HxCDF	<LOD	<LOD	<LOD	<LOD	<LOD
2,3,4,6,7,8-HxCDF	<LOD	<LOD	<LOD	<LOD	<LOD
1,2,3,4,6,7,8-HpCDF	1.10	1.10	<LOD	<LOD	<LOD
1,2,3,4,7,8,9-HpCDF	<LOD	<LOD	<LOD	<LOD	<LOD
OCDF	<LOD	<LOD	<LOD	<LOD	<LOD
Sum of PCDD/Fs	**23**	**26**	**4**	**6**	**5**
3,3',4,4',-TeCB(CB77)	35.00	56.00	21.00	50.00	11.00
3,4,4',5-TeCB(CB81)	2.00	2.40	0.31	5.80	0.72
3,3',4,4',5-PeCB(CB126)	6.00	16.00	2.70	1.70	<LOD
3,3',4,4',5,5'-HxCB(CB169)	2.00	3.40	1.60	2.60	1.00
2,3,3',4,4'-PeCB(CB105)	140.00	320.00	33.00	190.00	78.00
2,3,4,4',5-PeCB(CB114)	53.00	210.00	2.20	180.00	5.40
2,3',4,4',5-PeCB(CB118)	560.00	1,500.00	130.00	1,200.00	250.00
2',3,4,4',5-PeCB(CB123)	31.00	110.00	1.70	94.00	7.40
2,3,3',4,4',5-HxCB(CB156)	190.00	740.00	9.10	620.00	47.00
2,3,3',4,4',5'-HxCB(CB157)	46.00	120.00	4.00	120.00	20.00
2,3',4,4',5,5'-HxCB(CB167)	82.00	330.00	4.90	240.00	30.00
2,3,3',4,4',5,5'-HpCB(CB189)	15.00	34.00	5.90	24.00	5.90
Sum of dl-PCBs	**1,200**	**3,400**	**220**	**2,700**	**460**

Available information indicates that there is no production of PCBs in Ghana[5]. The main potential PCB-containing applications are transformers and capacitors for closed applications whereas plasticizers constitute the largest source for open applications of PCBs releases in Ghana. Other open applications may include certain paints, fire retardants and lubricants. There is however no statistics on national imports (including quantities and types) to allow the estimation of potential volumes of such uses. The sources of emissions of PCDD/Fs to air, water and residue are mainly due to uncontrolled combustion processes (particularly indiscriminate bush fires). Other sources of PCDD/Fs include medical wastes incineration, power generation/heating and transport (particularly in the urban areas where vehicular traffic is a problem). The present study is the first investigation on concentrations of PCDD/Fs and dl-PCBs in fish collected from Lake Volta, Lake Bosumtwi and the Weija Lake. The results indicate that the total concentrations of PCDD/Fs and dl-PCBs (i.e. sum of PCDD/Fs and dl-PCBs) in fish collected from the three lakes are relatively low with an average value of 3.4 pg WHO-TEQg^{-1} lipid wt. or 0.3 pg WHO-TEQg^{-1} wet wt. (upperbound) (Table 2). One recent study reported that the total concentration of PCDD/Fs and dl-PCBs (i.e. sum of PCDD/Fs and dl-PCBs) in human milk in the general population of Ghana were 6.07 ± 1.11 pg WHO-TEQg^{-1} lipid wt. (Clarke and Adu-Kumi, 2009). The reported total PCDD/Fs and dl-PCBs concentrations (i.e. sum of PCDD/Fs and dl-PCBs) in Ghanaian human breast milk were comparatively lower than those of the other participating countries of the WHO-UNEP Human Milk Studies[6].

Table 2: Concentrations of PCDD/F and dl-PCB congeners (pg WHO-TEQg^{-1} [a] of lipid wt.) in fish from Lake Volta, Lake Bosumtwi and Weija Lake

Concentrations of PCDD/F and dl-PCB congeners (pg WHO-TEQg^{-1} lipid wt.)	Average	Tilapia = 9		Catfish = 4	
		Max	Min	Max	Min
WHO-PCDD/F-TEQ (upperbound)[b]	2.7	3.4	0.9	1.1	0.8
WHO-PCDD/F-TEQ (mediumbound)[b]	2.7	3.3	0.8	1.1	0.5
WHO-PCDD/F-TEQ (lowerbound)[b]	2.7	3.3	0.7	1.1	0.5
WHO-dlPCBs (non-ortho) -TEQ (upperbound)[c]	0.7	1.7	0.3	0.2	0.1
WHO-dlPCB (mono-ortho) -TEQ (upperbound)[c]	0.0	0.1	0.0	0.1	0.0
WHO-dlPCBs-TEQ (upperbound)[c]	0.7	1.8	0.3	0.3	0.1
WHO-dlPCBs-TEQ (mediumbound)[c]	0.7	1.8	0.3	0.3	0.0
WHO-dlPCBs-TEQ (lowerbound)[c]	0.7	1.8	0.3	0.3	0.0
WHO-PCDD/F-PCB-TEQ (upperbound)[d]	3.4	5.2	1.2	1.4	0.9
WHO-PCDD/F-PCB-TEQ (mediumbound)[d]	2.7	3.3	0.8	1.1	0.5
WHO-PCDD/F-PCB-TEQ (lowerbound)[d]	2.7	3.3	0.7	1.1	0.5

[a]Calculated using WHO 2005 TEFs; [b]Sum of PCDD/F; [c]Sum of dl-PCBs; [d]Sum of PCDD/F and dl-PCBs

Explanations:
Upperbound: Use of LOQ for the contribution of each non-quantified congener to the TEQ
Mediumbound: Use of half of LOQ for the contribution of each non-quantified congener to the TEQ
Lowerbound: Use of zero for the contribution of each non-quantified congener to the TEQ
< [LOD]: Below limit of detection (LOD); < [LOQ]: Below limit of quantification (LOQ =3LOD)

The species-specific bioaccumulation of PCDD/Fs and dl-PCBs were observed. PCDD/Fs were higher in tilapia than in catfish at all locations, whilst for all locations dl-PCBs were higher in catfish than in tilapia , but as it indicated earlier, in this study, only muscle tissues concentrations of PCDD/Fs and dl-PCBs were measured (see Figure 1). There are no previous data to compare the present results with to indicate any decreasing or increasing time trends of PCDD/F and dl-PCB concentrations during the period of our study. The levels of PCDD/Fs and dl-PCBs in all fish samples for all locations are higher in the Weija Lake and Lake Bosumtwi, which are enclosed water bodies and also close to large population and industrial cities of Ghana, than levels in the Volta Lake (except for catfish for PCDD/Fs were slightly higher in Lake Volta). Causes of fish susceptibility to PCDD/Fs and dl-PCBs contamination also depends on the fat content by percentage of fish. Fishes with such characteristics nature of having high fat, which live near the coast and near the mouth of rivers such, as the Weija Lake, generally contain high concentrations of PCDD/Fs and dl-PCBs. Relatively big, fatty predatory fishes which are at the upper level of the food-chain have high concentrations of PCDD/Fs and dl-PCBs. In the absence of a Ghanaian commodity standard for dioxins and furans, data obtained in this study were compared against the EU standard: EU Amended Regulation (EC) No 199/2006 (which includes MLs for PCDD/Fs and combined MLs for PCDD/Fs and dl-PCBs in food). The concentrations in the regulation are expressed on a fresh weight basis and mean results (PCDD/Fs and dl-PCBs) are upperbound concentrations expressed as pg WHO-TEQg^{-1} (to 2 significant figures) [7]. The measured values in all instances were well below the permissible limits of both EU Regulation (EC) No 2375/2001 and the EU Amended Regulation (EC) No 199/2006. The results were, however, comparable with some recent studies world-wide and therefore constitute a potential health risk for the general population of Ghana.

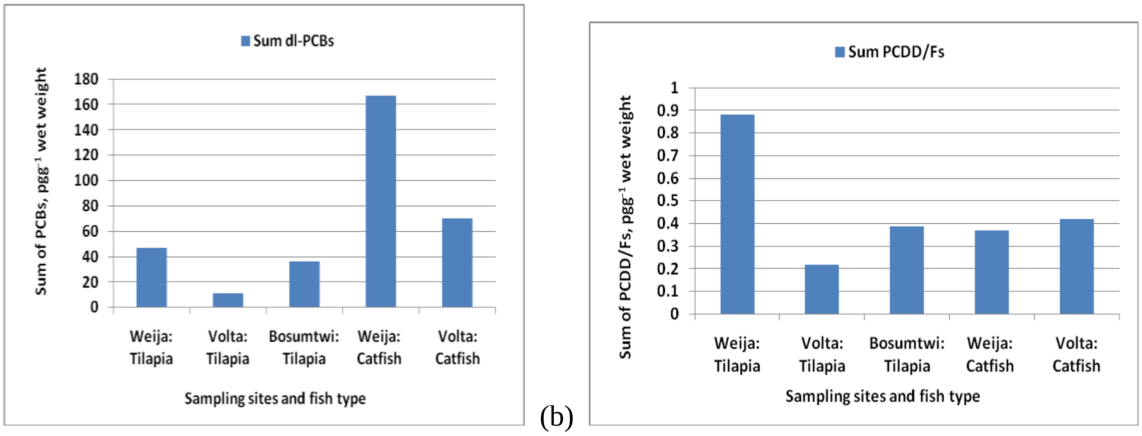

Fig. 1. Average concentrations of (a) dl-PCBs and (b) PCDD/Fs in tilapia and catfish according to sampling sites

The discussions on the levels of PCDD/Fs and dl-PCBs in this study were mainly based on comparisons with existing EU regulations and no toxicological assessments were made on this data. All measured values were well below the EU fish commodity standards or action levels. Almost all samples had detectable levels of PCDD/Fs and dl-PCBs. Although the detected levels of PCDD/Fs and dl-PCBs were well below the known action levels set by EU, they are however, comparable with the recent data of some developed countries. There is a potential health risk from PCDD/Fs and dl-PCBs for the general population of Ghana because fish is one of their important protein sources. It is therefore necessary to estimate the total intake of PCDD/Fs and dl-PCBs in particular, and to assess the health risks for general population of Ghana. Efforts should also be made to reduce the possible sources of emissions at the national level with a view to reducing total WHO-TEQ of PCDD/Fs and dl-PCBs in fish as the best means of controlling exposure to the general population from these environmental contaminants. Since this study only tested a limited number of samples, further monitoring should be considered by the appropriate bodies at the national level.

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