POLYCHLORINATED BIPHENYLS AND BROMINATED FLAME RETARDANTS IN FISH COLLECTED FROM FRESH WATER AND COASTAL REGIONS OF INDIA

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Introduction

Polychlorinated biphenyls (PCBs) were extensively used in electrical installations and various other industrial processes. Polybrominateddiphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are two classes of additive brominated flame retardants (BFRs) that are applied to various commoditiesto reduce the risk of ignition and burning. Significant amounts of PCBs and BFRs can also be released into the environment during manufacture, application, use and disposal through volatilization and leaching and also through particulate losses . These two groups of chemicals share similar toxic properties such as endocrine disruption, reproductive toxicity, developmental and neuro-behavioral defects and can cause cancer. They are bioaccumulative and have greater atmospheric transport potential. In addition, transformation of these compounds can produce more toxic compounds such as polyhalogenateddibenzodioxins and dibenzofurans. Although developed nations implemented regulations on the production, use, trade and disposal of these chemicals, developing countries including India are yet to start such initiatives. Even though no detailed information is available on the production and usage of PCBs and PBDEs in India, increasing industrialization may significantly contribute to the increasing usage of such chemicals.

In India, e-waste generation from domestic origin is increasing steadily along with the international input of end of life electronic wastes. Huge amount of e-waste has been imported and recycled in India without proper techniques which can cause severe health concerns. Recent studies suggested that developing countries have probably become the “hot spots” of organohalogen contamination. Dietary intake has significantly contributed to PCBs and PBDEs exposure, fish and shellfish being the major pathways for higher intake of PBDEs in human (Domingo et al., 2008). Although there is an extensive literature on the presence and fate of these contaminants in the aquatic environment and biota from many developed countries, there is little or no data on BFRs contamination in the fast growing nation, India. Therefore, the present study aims to give an overview of BFRs and PCBs contamination in various fish species along the coastal areas of two industrial cities and an inland town and compare the concentrations of PCBs and BFRs in wild and farmed fish. Additionally, human dietary exposure through the ingestion of contaminated fish was calculated. To our knowledge, this is the first assessment of human exposure to BFRs through fish consumption in India.

Materials and methods

Sample collection

Fish samples were collected from three different locations including the cities Mumbai and Chennai (marine fishes, n=21 pooled samples) and Sirkazhi (fresh water, n=20 (farmed 10 + wild 10) in India during 2009 (Fig. 1) andstored at -20°C in the Environmental Specimen Bank (es-Bank) of Ehime University until analysis.

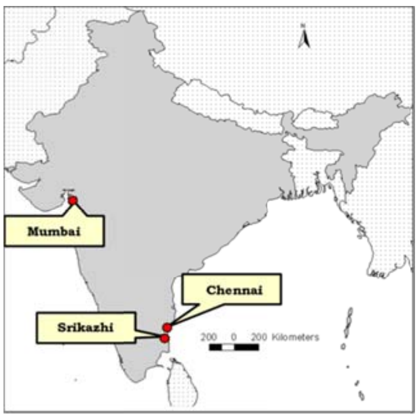

Fig. 1. Sampling locations

Chemical Analysis

Analysis of PCBs, PBDEs and HBCDs were carried out according to the method described elsewhere (Ueno et al., 2004), with slight modifications. Briefly, 5 g of freeze dried samples were extracted with acetone and hexane (1:1) in a high speed solvent extractor (SE-100, Mitsubishi Chemical Analytech). An aliquot of the extract was used to quantify the lipid content. The remaining extract was subjected to gel permeation chromatography, concentrated and passed through a glass column packed with activated silica gel and extracted with suitable solvents. PCBs and PBDEs were quantified using a gas chromatograph coupled with a mass spectrometer (GC-MS). HBCD isomers were quantified using a liquid chromatograph coupled with a tandem mass spectrometer.

Statistical analysis

Statistical analysis was performed using statistical software package R (R Foundation for Statistical Computing, Vienna, Austria) version 2.12.0. Principal component analysis (PCA) was performed to investigate the variation patterns of major PBDE and PCB congeners.

Results and discussion

Contamination status

PCBs and BFRs concentrations in fish samples varied widely among species/locations as shown in Table 1. Ranges and mean levels of PCBs were higher in all samples (430 and 20-2800 ng/g lipid wt.) than those of PBDEs (11 and 1.4-50 ng/g lipid wt.) and HBCDs (0.75 and nd-4.4 ng/g lipid wt.). We found similar pattern of distribution of these compoundsin Indian human breast milk (Devanathan et al., 2010) showing its even distribution in the environment and biota.

Table 1. Concentrations of PCBs and BFRs in fish from India

Location	Sample id	Scientific name	Common name	n	Lipid(%)	PCBs	PBDEs	HBCDs
Srikazhi	Cat-wd	*Catla catla*	Catla	4	1.9-2.6	60	3.0	0.0
Srikazhi	Cat-cul	*Catla catla*	Catla	4	1.6-3.4	210	15	0.0
Srikazhi	Varal-wd	*Channa marulius*	Great snakehead	4	1.2-2.1	20	5.2	0.0
Srikazhi	Varal-cul	*Channa marulius*	Great snakehead	4	1.0-3.9	190	7.4	0.0
Srikazhi	Carp-wd	*Hypophthalmichthys molitrix*	Silver carp	2	0.5-2.0	32	4.6	0.0
Srikazhi	Carp-cul	*Hypophthalmichthys molitrix*	Silver carp	2	0.4-2.0	52	9.9	0.0
Chennai	Duss acu	*Dussumieria acuta*	Rainbow sardine	4	0.7	130	10	0.77
Chennai	Sar lon-ch	*Sardinella longiceps*	Indian oil sardine	4	1.1	130	8.8	0.030
Chennai	Rast kan-ch	*Rastrelliger kanagurta*	Indian mackerel	4	1.3	85	19	0.46
Chennai	Day alb	*Daysciaena albida*	Two-bearded croaker	5	1.5	260	12	0.0
Chennai	Mug cep-ch	*Mugil cephalus*	Flathead mullet	4	2.1	1300	35	1.8
Chennai	Nib mac	*Nibea maculata*	Blotched croaker	4	1.6	130	2.0	3.0
Chennai	Thy mys	*Thryssa mystax*	Mustached anchovy	5	1.3	150	9.4	0
Mumbai	Bom duc	*Harpadon nehereus*	Bombay duck	3	1.2	370	12	2.0
Mumbai	Tuna	*Thunnus alalunga*	Tuna	1	0.7	72	8.7	1.1
Mumbai	Mug cep-mu	*Mugil cephalus*	Flathead mullet	2	4.7	1800	50	4.4
Mumbai	Pro dia	*Protonibea diacanthus*	Blackspot crocker	3	1.9	120	1.8	0.25
Mumbai	Coi duss	*Coilia dussumieri*	Coilia dussumieri	12	1.1	1100	18	0.0
Mumbai	OB	*Otolithoides biauritus*	Bronce croaker	3	5.2	340	2.3	0.0
Mumbai	'ast kan-mur	*Rastrelliger kanagurta*	Indian mackerel	2	1.3	310	6.0	2.4
Mumbai	Pam arg	*Pampus argenteus*	Silver pomfret	3	0.4	250	7.8	0.23
Mumbai	Scom gut	*Scomberomorus guttatus*	Indian king mackerel	1	1.3	180	7.5	0.0
Mumbai	Lep sav	*Lepturacanthus savala*	Silver ribbon fish	4	1.4	490	16	0.0
Mumbai	Ari mac	*Arius maculatus*	Spotted catfish	1	1.4	93	2.3	1.4
Mumbai	Nem jap	*Nemipterus japonicus*	Japanese threadfin bream	3	2.0	42	1.4	0.0
Mumbai	Sar lon-mur	*Sardinella longiceps*	Indian oil sardine	3	2.0	840	5.6	1.1
Mumbai	Ter jar	*Terapon jarbua*	Tiger-fish	4	2.4	2800	16	1.3

The median values of PCBs and PBDEs in marine fish samples (250 and 8.8 ng/g lipid wt.) were significantly higher than in fresh water species (56 and 6.3 ng/g lipid wt.). HBCDs were detected only in marine samples. This can be explained by the longer food chains in the marine ecosystem resulting in higher biomagnification and also due to the heavy pollution by persistent organic chemicals discharged from the industrial cities such as those in the present study (Mumbai and Chennai). On the other hand, freshwater fish collected in this study are mostly from small ponds in a small town (Sirkazhi) that has less likelihood of receiving continuous discharge from point sources. These results imply the presence of PCB sources mainly in urban and industrialized areas in India. Among the two big cities, significantly higher levels of PCBs were present in Mumbai (median: 320 ng/g lipid wt.) than Chennai (median: 130 ng/g lipid wt.) but PBDEs (10 and 7.6 ng/g lipid wt.) and HBCDs (0.46 and 0.66 ng/g lipid wt.) were in similar ranges in Mumbai and Chennai indicating possibly higher contamination of PCBs on the west coast thanin the east.

Concentrations of PCBs were relatively higher in benthic fishes than in pelagic species. This could be due to the exposure of benthic organisms with sedimentary PCBs via several direct and indirect routes.Elevated levels of PCBs, PBDEs and HBCDs were present in carnivorous fish than the planktanivores indicating that the feeding habits intervene in the accumulation process and also that lipophilic and highly stable compounds will be accumulated and magnified through food chain. Carnivorous fish feed mainly with small fish whereas herbivorous and detritivorous fish often feed on phytoplankton, zooplankton and bacteria. In addition metabolic capacities may also play a major role.

Comparatively higher levels of PCBs and PBDEs were found in fresh water farmed fish than wild fish such as *Catlacatla* (catla), *Channamarulius* (Snakehead), and *Hypophthalmichthysmolitrix* (Silver carp). Several studies have reported high levels of PCBs and PBDEs in farmed fish than wild fish.

Global comparison

Levels of PCBs in fish from India were comparable with Indonesia and China. However, contaminations of PCBs in fish from India were lower than industrialized nations such as and Australia (Kannan et al., 1992). Worldwide comparison of PCBs confirms that developed countries were more contaminated by PCBs than developing nations; implying higher persistency of PCBs combined with higher consumption in these industrialized nations. However, it is worthy to highlight here that India stands on top of PCBs contamination among developing countries.

In general, PBDEs contamination in fish in the present study was relatively lower when compared with other regions of the world, especially North America. This could be due to the heavier usage of Penta-BDE in North America than in Europe and Asia. During a global monitoring of PBDEs, Ueno et al. (2004) found low levels of contamination in skipjack tuna collected from Bay of Bengal. The Asian mussel watch program also reported relatively low concentrations of PBDEs in India (Ramu et al., 2007). Growing economic development andunprecedented urbanization increases the consumption of PBDEs. In addition, export of electronic waste (e-waste) from developed counties is creating a significant new source for environmental PBDEs in developing countries including India.

HBCDs were not detected in most samples analyzed in this study and their levels in India were lower than many reported values on fish. Similar low concentrations of HBCDs were found in human breast milk from India (Devanathan et al., 2010). It is obvious that the HBCDs pollution in Europe has been spreading rapidly than in the developing countries like India.

Composition of PCBs and BFRs

In the present study, the congener profile of PCBs was dominated by higher chlorinated CBs, irrespective of species and locations. Homologue pattern was abundant with hexa-CBs, followed by hepta-CBs and penta-CBs, in that order, in both fresh water and marine fishes. PCB congener residue profiles are influenced by many factors (e.g. exposure source(s), species difference, degradation rates, transportation differences). This pattern supports the already known patterns where there was relatively low metabolism of high chlorinated PCB congeners in fish.PCB153 is one of the major components of commercial PCB mixtures (e.g., 4.26% in Aroclor 1254 and 10.20% in Aroclor 1260) and it is one of the most frequently reported PCB congeners in environmental samples.

Relatively high levels of lower chlorinated congeners including CB-28, -52, -70 in freshwater fishes including *Channamarulius,Mugilcephalus, Teraponjarbua* could be due to the difference in sources which may strongly affect the differences in congener profiles. In general, it appears that in most fish samples, congeners 153, 138 and 180 were dominant as they are highly persistent and are not metabolized by fish as also seen by Devanathan et al. (2010) in human breast milk from Indiaindicating that pollution in India may be mainly attributed to the technical mixtures similar to Aroclor 1260 and Aroclor 1254. However, relative portions of different congeners are not always exactly the same as in those technical mixtures as PCB congeners are degraded or metabolized at different rates.

PBDEs congener pattern was dominated by lower brominated congeners such as BDE-47 (53%) followed by BDE-99 (9%) and BDE-100 (8%) in both fresh water and marine fish (Fig. 2). The relative contributions of BDE-99 and 100 to PBDE concentrations were often different between fish species. In the present study, BDE-153 and -154 were found at low concentrations in most fish samples and also higher brominated congener, BDE-209 was found at relatively high levels in some fishes that mostly live in benthic areas possibly relating to their benthic living habits, which make them more easily exposed to particle-bound highly brominated congeners.

In order to find out the differences and similarities in PBDE profile among samples, principal component analysis (PCA) of concentrations of PBDE congeners was performed. The factor score plot for PC1 (43%) and PC2 (16%) were shown in Fig. 2. It was found that *Channamarulius,Catlacatla,Teraponjarbua* contained higher levels of lower brominated congeners, whereas *Mugilcephalus* had high contribution of BDE-209 which may explain its benthic habitat. Additional studies are required to determine if these congeners come from debromination processes of higher brominated PBDEs or due to their bioavailability potential.

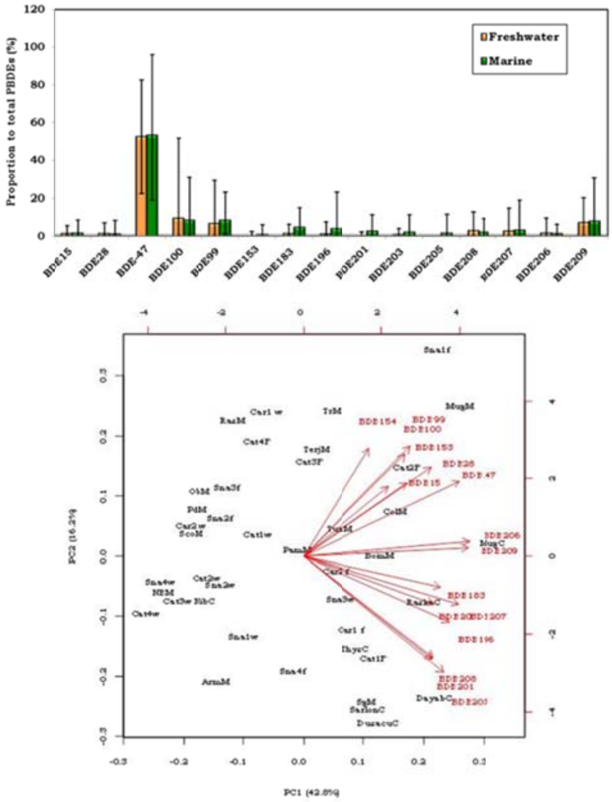

Fig. 2. PBDE congener pattern with principle component analysis plot

5.3.4. Assessment of Health risk via fish consumption

Daily intake of PCBs and PBDEs through fish consumption was calculated using the average daily consumption rates of fish in different countries, suggested by FAO and concentrations observed in this study. Human dietary intake of PCBs via fish analyzed in this study, for an adult Indian (0.11µg/person/day) was well below the acceptable daily intake proposed by FAO/WHO/health Canada (60 µg/person/day) indicating minimal health risk. Compared with other studies, the dietary intake of PCBs in India via fish were lower than in developed nations such as Japan (17 µg/person/day) and Australia (3.0 µg/person/day) but higher than Cambodia (0.007 µg/person/day) and Thailand (0.091 µg/person/day).

The present dietary intake of PCBs (0.11µg/person/day) via fish by Indians was higher than the fish samples collected on 1989 (0.036 µg/person/day)(Kannan et al., 1992). This increasing trend may also be due to the increasing e-waste activities, ship breaking etc. during recent years in India. Hazard Quotient (HQ) calculated using daily intake value and reference dose proposed by US-EPA and Health Canada for PBDEs congeners and total PCBs were below one indicating the minimal heath risk by these contaminants in India. However, fish could also contain many other harmful chemicals of concern at sufficiently high levels and therefore combined toxicological studies are needed to address the safety issue of fish consumption.

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