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Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers in Fishes Collected from Tam Giang-Cau Hai Lagoon, Vietnam

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Abstract—Various fish species including freshwater, brackish water and migrant fishes collected from Tam Giang-Cau Hai lagoon were analyzed for polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) to assess their contamination status in the lagoon. PCBs and PBDEs were detected in all samples with mean concentrations from 63 to 150 ng/g lipid wt and from 2.6 to 26 ng/g lipid wt, respectively. PCB levels were variable among fish species with a similar congeners pattern showing a historical usage, ubiquitous and uniform emission of PCBs in the studied region. In contract, the highest PBDEs level was found in freshwater fishes, followed by brackish water fishes and migrant fishes indicating freshwater as a proper source of PBDEs. BDE-209 was detected in most of the samples and this may have resulted from their benthopelagic/demersal living habit. This study provided the first insight into contamination by both PCBs and PBDEs in fishes from Tam Giang-Cau Hai lagoon, and the results suggest the need for further monitoring on these contaminants in Central Vietnam.

Keywords: polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), fishes, Tam Giang-Cau Hai Lagoon

INTRODUCTION

Despite restrictions/bans on their manufacture and use in most industrialized/developed countries since the 1970s, polychlorinated biphenyls (PCBs) can still be measured in environmental samples due to their highly lipophilic properties which make them persist in the environment, bioaccumulate through the food chain and cause potential toxic risks to humans (Domingo and Bocio, 2007). Due to their widespread presence in the environment and their reported possible adverse health effects, polybrominated diphenyl ethers (PBDEs) have become the subject of intensive research (Shaw *et al.*, 2010). PBDEs can reach the environment through leaching during production and application processes, through volatilization and leaching during use and through particulate losses

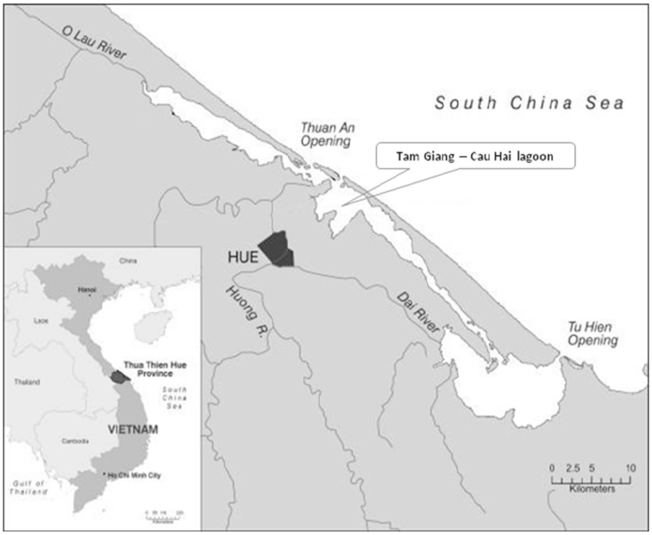

Fig. 1. Map showing the sampling location.

during use and disposal (Darnerud *et al.*, 2001). In this way, point sources often lead to contamination of adjacent aquatic systems and to increased levels in aquatic organisms, such as fish. Most of the scientific publications regarding contamination, potential sources, and pathways of PBDEs in Asia have been limited to some East Asian countries. Very few studies have been carried out in other parts of Asia, including Southeast Asia, where a number of rapidly developing countries such as Vietnam are situated.

Tam Giang-Cau Hai lagoon is the largest lagoon in Southeast Asia, lies along the coastal line of Thua Thien Hue province and plays a vital role in lives of local people and socio-economic development of the province. Municipal and industrial wastewaters which consist of various anthropogenic pollutants are discharged directly without any treatment to the lagoon-river system, probably causing several adverse environmental consequences and increased human health risk to local communities. Fish is a suitable indicator for environmental pollution monitoring because they concentrate pollutants in their tissues directly from water, and also through their diet, thus enabling the assessment of transfer of pollutants through the trophic web. Data on the presence and distribution of toxic pollutants in fish and especially edible fish species are therefore important from ecological and human health perspectives. Humans are exposed inadvertently to PCBs and BFRs through numerous sources, of which the consumption of contaminated fish is one of the most important pathways. The present study evaluated concentrations of PCBs, PBDEs and HBCDs in various fish species collected from Tam Giang-Cau Hai lagoon, Vietnam to understand their contamination status, geographical variation and contaminants profiles.

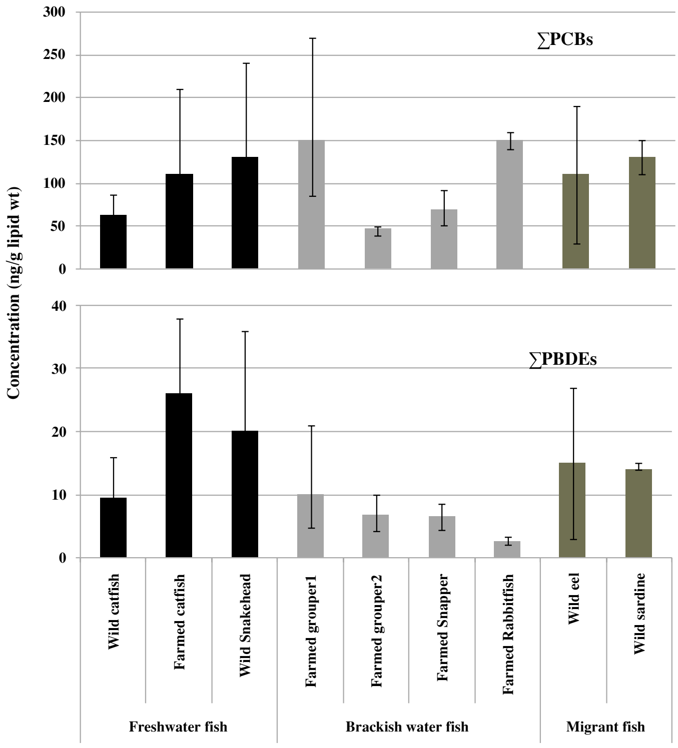

Fig. 2. Concentrations of PCBs and PBDEs in fish samples from Tam Giang-Cau Hai lagoon.

MATERIALS AND METHODS

Sample collection

Fish species ($n = 31$; freshwater, brackish water and migrant fish having wild and farm-raised) were collected from Tam Giang-Cau Hai lagoon, Vietnam during September 2008 (Fig. 1) and were analyzed for PCBs and PBDEs in this study as individual and/or pooled samples. The individual fish species were broadhead catfish (*Clarias macrocephalus*, farmed, $n = 4$), walking catfish (*Clarias batrachus*, wild, $n = 3$), snakehead (*Channa striata*, wild, $n = 3$), snapper (*Lutianus johnii*, farmed, $n = 5$), grouper (*Epinephelus coioides*, farmed, $n = 3$), grouper (*Ephinephelus sexfasciatus*, farmed, $n = 5$) and eel (*Anguilla japonica*, wild, $n = 4$). In addition, pooled samples of sardine (*Nematalosa nasus*, wild, $n = 2$) and white spotted rabbit fish (*Siganus canlicalatus*, farmed, $n = 2$) were studied. The collected samples were shipped frozen to the Center for Marine Environmental Studies laboratory in Japan and stored at –20°C in the Environmental Specimen Bank (*es*-Bank) of Ehime University (Tanabe, 2006) until analysis.

Chemical analysis

Analysis of PCBs (62 congeners) and PBDEs (42 congeners) were carried out following the procedure described elsewhere (Takahashi *et al.*, 2010; Eguchi *et al.*, 2011). Briefly, 20–30 g wet weight (ww) of muscle tissues were homogenized and freeze-dried, and 5 ng of internal standards of PCBs and PBDEs were spiked as surrogates and then these samples were extracted using high-speed solvent extractor (SE-100; Mitsubishi Chemical Analytech Co., Ltd., Japan) at a flow rate of 10 mL/min with a mixture of acetone and hexane (1:1 v/v) at 35°C for 30 min. The extract was then subjected to gel permeation chromatography (GPC; Bio-Beads S-X3, Bio-Rad Laboratories, CA, 2 cm i.d. and 50 cm length) for lipid removal and eluted with mixture of 50% hexane/dichloromethane (1:1). The GPC fraction containing PCBs and PBDEs were concentrated and passed through 4 g of activated silica gel (Wakogel DX, Wako Pure Chemical Industries Ltd., Japan). Identification and quantification of PCBs and PBDEs in the first fraction of 5% dichloromethane in hexane were done using gas chromatography combined with mass spectrometry (GC-MS). Procedural blanks were analyzed simultaneously with samples to check for interference or contamination from solvents and glassware. The concentrations of PCBs and PBDEs in fish samples were expressed in ng/g lipid weight basis unless otherwise specified.

RESULTS AND DISCUSSION

Levels, distribution and profile of polychlorinated biphenyls

PCBs were detected in all samples with the highest level among contaminants analyzed. The sum of 62 congeners (∑PCBs) concentrations varied widely from 63 to 150 ng/g lipid wt., with an overall mean of 110 ng/g lipid wt. (Fig. 2). The observed levels of the PCB congeners from all the fish species were not statistically significant. It is predicted that every fish species contributes differently to the overall contamination pattern due to the diversity in the collected species and their physiological differences, such as lipid content, feeding habit and degree of bioaccumulation for various contaminants.

The levels of PCBs found in our study were comparable with others found in China (Nie *et al.*, 2006), but much lower than those reported in Indonesia, Belgium and USA (Johnson-Restrepo *et al.*, 2005; Sudaryanto *et al.*, 2007; Roosens *et al.*, 2008). The mean concentration of this study was higher than in pangasius catfish from Can Tho, Vietnam (Minh *et al.*, 2006), while comparable with other studies in walking catfish and snakehead collected from Thi Nghe-Sai Gon river, Vietnam (Vinh, 2009), probably due to the corresponding background residue levels in the environment and/or species-specific differences in absorption, egestion, disposition and metabolism (Nie *et al.*, 2006).

Homologues profile of all fish species in this study was dominated by penta-, hexa- and hepta-CBs (Fig. 3). This profile was similar with one observed in Can Tho dumpsite catfish in Vietnam (Minh *et al.*, 2006). In general, higher chlorinated congeners were accumulated greater than lower chlorinated congeners

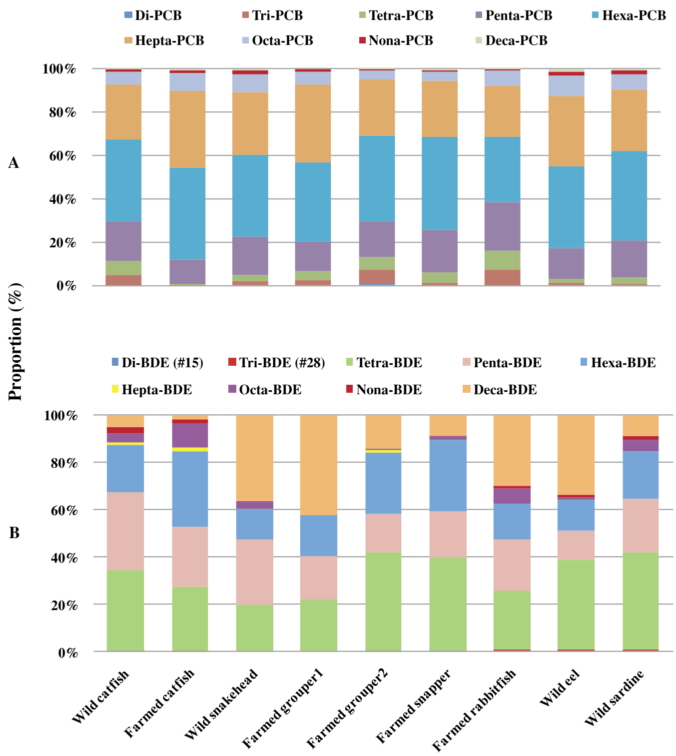

Fig. 3. Profile of PCBs (A) and PBDEs (B) in fish samples from Tam Giang-Cau Hai lagoon.

in almost all the samples. Due to the number and position of chlorine atoms, PCB congeners do not follow the same metabolic pathway which results in the formation of different metabolites and in differences in accumulation patterns and persistence of PCBs (Weijs *et al*., 2009). PCBs with fewer chlorine atoms tend to be more easily metabolized while large number of chlorine atoms are associated with increased resistance to biodegradation, which can increase bioaccumulation in biota. This profile in all samples may show the historical usage, ubiquitous and uniform emission of PCBs in the studied area.

Levels, distribution and profile of polybrominated diphenyl ethers

PBDEs were detected in all samples suggesting their widespread contamination in the lagoon environment, ranged from 2.6 to 26 ng/g lipid wt., with overall mean concentration of 12 ng/g lipid wt. PBDE levels were found high in the freshwater fishes followed by migrant and brackish water fishes (Fig. 2). High concentrations of PBDEs in the freshwater fishes may suggest their habitats were in the polluted areas such as major urban and dumpsite areas and/or pools around industrial zones, indicating that freshwater from Tam Giang-Cau Hai

Lagoon in Vietnam may also have pollution sources of PBDEs. The lowest concentration was observed in the brackish water fish (rabbitfish), which may be due to herbivorous feeding habit. Rabbitfish often feed on phytoplankton, benthic algae in addition to synthetic feeds. Whereas an another herbivorous species such as sardine had higher concentration, probably related to their physiological differences such as lipid decrease after migrating from open sea to lagoon and variety in diet composition (zooplankton, crustacean larvae and to some extent fish eggs), and/or exposure to contaminants inside the lagoon-river system.

Overall mean concentrations of PBDEs (12 ng/g lipid wt.) in this study were comparable with others found in China, Chile and USA (Johnson-Restrepo *et al.*, 2005; Montory and Barra, 2006; Tian *et al.*, 2010), but much lower than those reported for marine and freshwater fishes in Taiwan, Europe, North America and Belgium (Hites, 2004; Peng *et al.*, 2007; Roosens *et al.*, 2008). The mean concentration of this study was comparable with previously reported in Can Tho, Southern Vietnam for pangasius catfish (Minh *et al.*, 2006).

PBDE congener profiles in all samples were dominated by tetra-, penta- and hexa-BDEs (Fig. 3) similar to patterns observed in freshwater and marine fishes from other regions of the world (Hites, 2004; Peng *et al.*, 2007). Decabrominated diphenyl ether (BDE-209) was detected in most of the samples. It has been reported that BDE-209 is not bioaccumulative due to its large molecular size (Minh *et al.*, 2006), rapid elimination and short half-lives in biota (2.4 days in rat, 8–13 days in grey seals, 15 days in human) (Sandholm *et al.*, 2003, Thomas *et al.*, 2005, Thuresson *et al.*, 2006). However, many recent studies reported the presence of BDE-209 in organisms, including fish, invertebrates and birds suggesting that BDE-209 is in fact bioaccumulable (Tian *et al.*, 2010). Thus, there is a great risk of exposure to BDE-209 by contact with sediment for benthic fish species in our study which live and prey on or near sediment bottom. Since in many aspects the fate and the behavior of BDE-209 are poorly understood, it is essential to study the mechanisms of transfer of BDE-209 into fish from the sediment.

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REFERENCES

Darnerud, P. O., G. S. Eriksen, T. Johannesson, P. B. Larsen and M. Viluksela (2001): *Environ. Health Perspect.*, **109**, 49–68.

Domingo, J. L. and A. Bocio (2007): Levels of PCDD/PCDFs and PCBs in edible marine species and human intake: a literature review. *Environ. Int.*, **33**, 397–405.

Eguchi, A., T. Isobe, K. Ramu and S. Tanabe (2011): Optimisation of the analytical method for octa-, nona- and deca-brominated diphenyl ethers using gas chromatography-quadrupole mass spectrometry and isotope dilution. *Int. J. Environ. Anal. Chem.*, **91**, 348–356.

Hites, R. A. (2004): Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.*, **38**, 945–956.

Johnson-Restrepo, B., K. Kannan, R. Addink and D. H. Adams (2005): Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. *Environ. Sci. Technol.*, **39**, 8243–8250.

Minh, N. H., T. B. Minh, N. Kajiwara, T. Kunisue, H. Iwata, P. H. Viet, N. P. C. Tu, B. C. Tuyen and S. Tanabe (2006): Contamination by polybrominated diphenyl ethers and persistent organochlorines in catfish and feed from Mekong River Delta, Vietnam. *Environ. Toxicol. Chem.*, **25**, 2700–2709.

Montory, M. and R. Barra (2006): Preliminary data on polybrominated diphenyl ethers (PBDEs) in farmed fish tissues (*Salmo salar*) and fish feed in Southern Chile. *Chemosphere*, **63**, 1252–1260.

Nie, X. P., C. Y. Lan, T. C. An, K. B. Li and M. H. Wong (2006): Distribution and congener patterns of PCBs in fish from major aquaculture areas in the Pearl River Delta, South China. *Hum. Ecol. Risk Assess.*, **12**, 363–373.

Peng, J. H., C. W. Huang, Y. M. Weng and H. K. Yak (2007): Determination of polybrominated diphenyl ethers (PBDEs) in fish samples from rivers and estuaries in Taiwan. *Chemosphere*, **66**, 1990–1997.

Roosens, L., A. Dirtu, G. Goemans, C. Belpaire, A. Gheorghe, H. Neels, R. Blust and A. Covaci (2008): Brominated flame retardants and polychlorinated biphenyls in fish from the river Scheldt, Belgium. *Environ. Int.*, **34**, 976–983.

Sandholm, A., B. M. Emanuelsson and E. K. Wehler (2003): Bioavailability and half-life of decabromodiphenyl ether (BDE-209) in rat. *Xenobiotica*, **33**, 1149–1158.

Shaw, S. D., A. Blum, R. Weber, K. Kannan, D. Rich, D. Lucas, C. P. Koshland, D. Dobraca, S. Hanson and L. S. Birnbaum (2010): Halogenated flame retardants: do the fire safety benefits Justify the Risks? *Rev. Environ. Health*, **25**, 261–305.

Sudaryanto, A., I. Monirith, N. Kajiwara, S. Takahashi, P. Hartono, I. Muawanah, K. Omori, H. Takeoka and S. Tanabe (2007): Levels and distribution of organochlorines in fish from Indonesia. *Environ. Int.*, **33**, 750–758.

Takahashi, S., T. Oshihoi, K. Ramu, T. Isobe, K. Ohmori, T. Kubodera and S. Tanabe (2010): Organohalogen compounds in deep-sea fishes from the western North Pacific, off-Tohoku, Japan: Contamination status and bioaccumulation profiles. *Mar. Pollut. Bull.*, **60**, 187–196.

Tanabe, S. (2006): Environmental specimen bank in Ehime University (*es*-Bank), Japan for global monitoring. *J. Environ. Monit.*, **8**, 782–790.

Thomas, G. O., S. E. W. Moss, L. Asplund and A. J. Hall (2005): Absorption of decabromodiphenyl ether and other organohalogen chemicals by grey seals (*halichoerus grypus*). *Environ. Pollut.*, **133**, 581–586.

Thuresson, K., P. Hoglund, L. Hagmar, A. Sjodin, A. Bergman and K. Jakobsson (2006): Apparent half-lives of hepta- to decabrominated diphenyl ethers in human serum as determined in occupationally exposed workers. *Environ. Health Perspect.*, **114**, 176–181.

Tian, S., L. Zhu and M. Liu (2010): Bioaccumulation and distribution of polybrominated diphenyl ethers in marine species from Bohai Bay, China. *Environ. Toxicol. Chem.*, **29**, 2278–2285.

Vinh, N. N. (2009): thèse No. 4520, Ecole Polytechnique Federale De Lausanne.

Weijs, L., A. C. Dirtu, K. Das, A. Gheorghe, P. J. Reijnders, H. Neels, R. Blust and A. Covaci (2009): Inter-species differences for polychlorinated biphenyls and polybrominated diphenyl ethers in marine top predators from the Southern North Sea: Part 1. Accumulation patterns in harbour seals and harbour porpoises. *Environ. Pollut.*, **157**, 437–444.

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