EMERGING HALOGENATED FLAME RETARDANTS IN COASTAL REGION OF CHINA

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Introduction

Halogenated flame retardants (HFRs) are a class of structurally diverse chemicals including chlorinated and brominated derivatives which are widely applied to household and industrial products such as textiles, plastics, furniture, and electronic products to inhibit or resist the spread of fire[1,2]. A well-known example of these is polybrominated diphenyl ethers (PBDEs) of which Penta- and Octa-BDE have been added to the Persistent Organic Pollutants (POPs) list of the Stockholm Convention due to their persistence, toxicity, bioaccumulation and long-range transport potential[3]. Since the worldwide restriction on the production and use of PBDEs[1], market demand for these compounds is expected to decline, whereas that for its alternatives is projected to increase.

In recent decades, China has been the fastest-growing country in the Asia-Pacific region in terms of population and economic development. Coastal environment of China has been undergoing strong modifications due to rapid urbanization and industrialization. These may increase the demand for flame retardants used in the manufacture of products for both domestic use and export, so it is not surprising that huge amounts of HFRs are found in this region.

A number of emerging HFRs are recently detected in the environment and the presence of several of these new chemicals in biota indicates that they are bioavailable and can be absorbed and bioaccumulated. However, the information regarding the environmental occurrence, distribution and fate of these chemicals is still scanty. Previous monitoring studies on eggs of two species of waterbirds[4], little egrets (*Egretta garzetta*) and black-crowned night herons (*Nycticorax nycticorax*), and two species of marine mammals[5], the Indo-Pacific humpback dolphin (*Sousa chinensis*) and finless porpoise (*Neophocaena phocaenoides*) from South China revealed the occurrence of elevated levels of PBDEs and hexabromocyclododecanes (HBCDs) in the Chinese coastal region. Detection of bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), in blubber samples of marine mammals indicated the presence of a potential source of these new brominated flame retardants in Pearl River Delta region. This has led to the suspicion that similar types of non-PBDE HFRs may be extensively used in the estuarine areas, and raises our attention on the status of these new chemicals in Chinese coastal waters.

Accordingly, the present study was undertaken to address the occurrence and spatial variations of PBDEs and twelve non-PBDE flame retardants including HBCDs, 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (TBECH), dechlorane plus (DPs), hexabromobenzene (HBB), decabromodiphenyl ethane (DBDPE), TBPH, 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), TBB, pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), hexachlorocyclopentadienyldibromocyclooctane (HCDBCO) and 2,3-Dibromopropyl-2,4,6-tribromophenyl ether (DPTE) in the marine environment of the China by analyzing the surface sediment, marine fishes, and the blubber of the Indo-Pacific humpback dolphin and finless porpoise from Chinese coastal region.

Materials and methods

Surface sediment samples (upper 2-3 cm) were collected by stainless steel sampling device during a scientific expedition cruise in the East China Sea and South China Sea conducted in 2011 and 2012. Stranded specimens of dolphins and porpoise were collected in Hong Kong, China, between 2003 and 2012. Two species of marine fish namely large yellow croaker (*Pseudosciaena crocea*) and sliver pomfret (*Pampus argenteus*) were collected from ten Chinese coastal cities in 2008 (Figure 2). All the samples were freeze-dried immediately after collection and stored at -20℃ until analysis. Pretreatment of HFRs analysis was accomplished by use of previously established methods[4-6] with modifications. Briefly, $^{13}C_{12}$-labeled HFR standards were added to each sample which was then extracted by accelerated solvent extractor (ASE200, Dionex). Copper powder was used to remove elemental sulfur in sediment and lipids of biological samples were removed by use of gel permeation chromatography (GPC). The concentrated fraction was then transferred and further purified by elution through multilayer silica/alumina column. $^{13}C_{12}$-labeled BDE139 was added as the recovery spike and deuterated HBCDs (α-, β- and γ-HBCD-*d*18) were spiked into the concentrated fraction prior to GC analysis and LC-MS/MS analysis, respectively.

Instrumental analysis of the HFRs was performed based on the analytical method by Zhou et al[7] with modifications. Identification and quantification were performed using a liquid chromatography-tandem mass spectrometer system (LC-MS/MS) consisting of an Agilent 1290 Infinity LC (Agilent Technologies, Palo Alto, CA) coupled to AB SCIEX QTRAP® 5500 LC-MS-MS system with an atmospheric pressure chemical ionization (APCI) interface. A Zorbax SB-C18 column (2.1mm×100mm, 1.8µm; Agilent Technologies, Palo Alto, CA) was used for the chromatography separation. Recoveries of $^{13}C_{12}$-labeled PBDEs, HBCDs, HBB, BTBPE and DBDPE in all samples were between 64% to 113%; matrix spike recoveries of BEHTBP, α- and β-TBECH, γ- and δ-TBECH, EHTBB, PBEB, PBT, *anti*-DP, *syn*-DP and HCDBCO ranged between 69-97%; the recoveries for BDE-47, -99, -100, -153,-154, -183 and -209 in NIST SRM1944 ranged between 61-126%, as compared with the certified values.

Results and discussion

Concentrations and profiles of halogenated flame retardants in the surface sediment samples

In the present study, all thirteen HFRs were detected in the surface sediment samples collected from Pearl River Delta (PRD) and Yangtze River Delta (YRD), with the exceptions of DPTE, HBB, PBEB, and PBT which were not detected in the YRD samples. HCDBCO was undetectable in all of the sediment samples. Among the HFR investigated, PBDEs and DBDPE were the most frequently detected and levels of PBDEs were the most predominant in sediment samples collected from PRD and YRD, and then followed by DBDPE (Figure 1). Composition profile of other non-PBDE HFRs found in the two estuaries varied geographically. For instance, percentage contribution of HBCDs detected in PRD samples appeared to be higher than those of YRD, whereas TBECH was higher in YRD. Comparisons of HFR concentrations in surface sediment between the two estuaries showed that one to two order of magnitudes higher levels were present in the samples collected from PRD. The observed geographical variations of HFR profile and concentration in surface sediment may be attributed to the differences in the quantities of HFRs used in the different locations, possibly reflecting the dissimilar developmental phases between the two coastal regions. PRD have been subjected to intense economic and industrial activities since 1980. This has turned the PRD region into one of the biggest production bases for

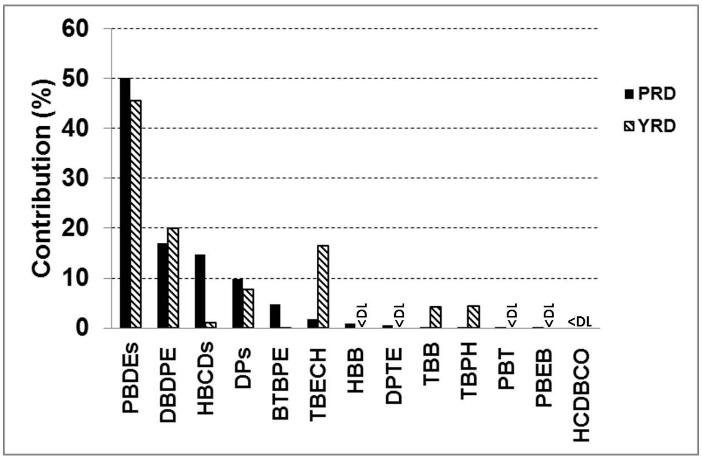

Figure 1. Percentage contribution of HFRs in the sediment samples from Pearl River Delta (PRD) and Yangtze River Delta (YRD) (<DL: below detection limit).

textiles, electronics and household goods industries in the world. The longer history of extensive industrial development around the PRD areas has apparently resulted in higher levels of HFRs found in the PRD marine environment compared to the YRD marine environment.

PBDEs and HBCDs in marine fishes

Concentrations of two species of commercial fish, yellow croakers and silver pomfrets from ten cities along the coastline were analyzed and the results revealed the widespread occurrence of PBDEs and HBCDs in the Chinese coastal regions (Figure 2). Among the three HBCD isomers (α-, β- and γ-HBCD) in all fish samples, the α-isomer showed a remarkable predominance, ranging from 88% to 100% of total contribution, indicating its higher bioaccumulative potential. The relatively higher levels of HBCDs in northern part of China than that of central China were observed and these were possibly related to human activities. Serious pollution of Bohai Bay waters by industrial and municipal effluents has occurred over the past two decades[8]. In addition, there is an important HBCD production base in the Laizhou Bay of Bohai[9] which is closer to Dalian. In general, the two most frequently detected HFRs, PBDEs and HBCDs, their levels present in fishes along the southern part of China were the highest as compared with the samples from northern and central coastal regions. These results were in good agreement with the higher levels of HFRs detected in the PRD surface sediment samples.

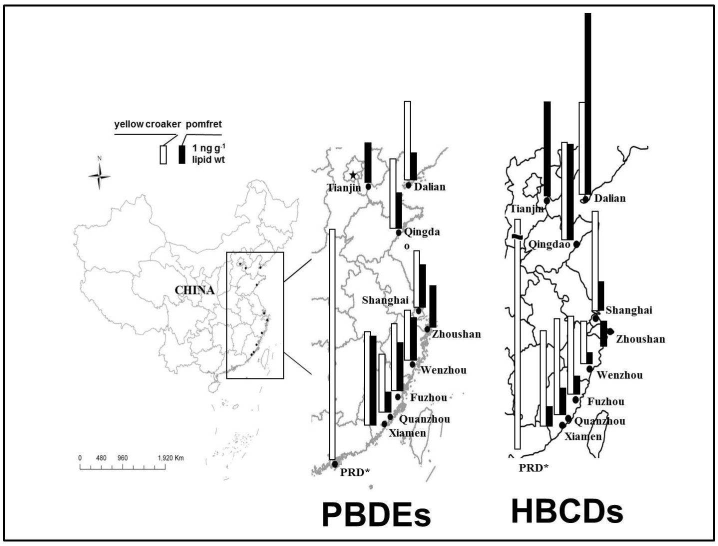

Figure 2. Map showing sampling locations and mean total concentrations of PBDEs and HBCDs in the marine fishes.

HFRs levels and composition profiles in marine mammals

Composition profiles and levels of thirteen HFRs in the blubber samples of two species of marine mammals, Indo-Pacific humpback dolphins and finless porpoises from the Hong Kong were investigated. Of the HFRs analyzed, PBDEs were the most predominant in the blubber samples of the two species of marine mammals, and then followed by HBCDs. Other non-PBDE HFRs including TBECH, DPs, HBB, DBDPE, TBPH, BTBPE, TBB, PBEB, PBT, HCDBCO and DPTE were all detected in both cetacean species (Figure 3). PBDEs and HBCDs extensively occurred in various environmental samples and exposure of wildlife and human to these compounds has been associated with various adverse effects such as immunotoxicity, endocrine

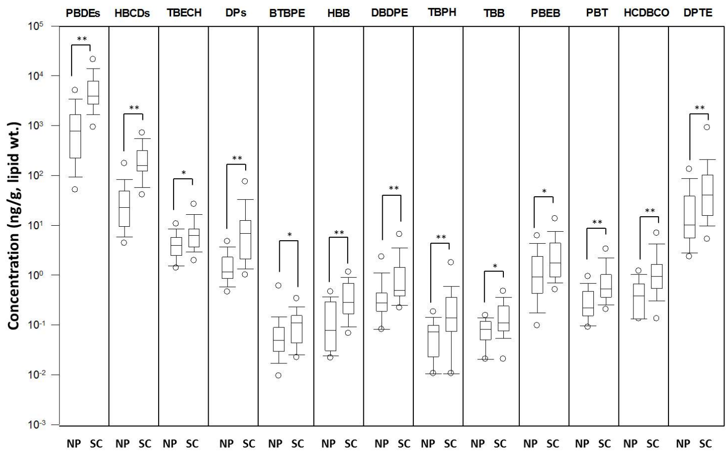

Figure 3. Comparison of the concentrations of HFRs in finless porpoise (NP) and Indo-Pacific humpback dolphin (SC) from South China. (* and ** indicate significance at the level $p<0.05$ and $p<0.001$, respectively,)

disruption, developmental and reproductive toxicity[10]. The occurrence of the other non-PBDEs HFRs in the blubber of the two cetacean species indicated that all these eleven non-PBDE HFRs were bioavailable and some of these, such as DPs, DPTE and TBECH, exhibited relatively high bioaccumulation potential in these two species of marine top predators. Levels of HFRs were significantly higher in dolphins than in porpoises (Figure 3), with the exceptions of TBPH, HBB, TBB and PBT which were higher in porpoises. The distribution patterns of dolphins and porpoises tend not to overlap; the dolphin is generally restricted to the estuarine northwestern waters of Hong Kong, whereas the porpoise is found in eastern waters. Regardless of potential species-specific differences, contaminant concentrations in the blubber of dolphins indicate that northwestern waters of Hong Kong are more contaminated by most of the analyzed HFRs than the eastern waters.

The present study indicated the widespread occurrence of non-PBDE HFRs in sediment and biological samples along the Chinese coastline. In addition, relatively high concentrations of these HFRs were found in the top predators of the marine food chain. However, the exposure pathways and accumulation patterns of these contaminants in the marine environment are still unclear, and information on their fate and effects are very limited. Further investigation of these topics is warranted.

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References
1. Covaci A, Harrad S, Abdallah MAE, Ali N, Law RJ, Herzke D, de Wit CA. (2011); *Environ Int.* 37: 532-66.
2. de Wit CA, Herzke D, Vorkamp K. (2010); *Sci Total Environ.* 408(15): 2885-918.
3. http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx
4. Lam JCW, Murphy MB, Wang Y, Tanabe S, Giesy JP, Lam PKS. (2008); *Environ Sci Technol.* 42(16): 6296-302
5. Lam JCW, Lau RKF, Murphy MB, Lam PKS. (2009); *Environ Sci Technol.* 43(18): 6944-9
6. Ramu K, Isobe T, Takahashi S, Kim EY, Min BY, We SU, Tanabe S. (2010); *Chemosphere*. 79: 713-9
7. Zhou SN, Reiner EJ, Marvin C, Helm P, Riddell N, Dorman F, Misselwitz M, Shen L, Crozier P, MacPherson K. (2010); *Anal Bioanal Chem.* 396: 1311-20
8. Meng W, Qin YW, Zheng BH, Zhang L. (2008); *China J Environ Sci.* 20: 814-9
9. Wang YW, Cai YQ, Jiang GB. (2010); *Scientia Sinica (Chimica)* 40, 99-123 (in Chinese)
10. Shaw SD, Berger ML, Weijs L, Covaci A. (2012); *Environ Int.* 44: 1-6 (and references therein)