PBDEs IN WATER AND AQUATIC BIOTA OF THE PEARL RIVER ESTUARY, SOUTH CHINA

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Abstract Water and aquatic organisms from the Pearl River Estuary have been sampled and analyzed for a suite of ten polybrominated diphenyl ether (PBDEs) congeners. The dissolved PBDE concentrations ranged from 2.5-128 pg/L. The dissolved PBDE concentrations in dry season were significantly higher than those in flood reason. The concentrations of PBDEs in organisms varied from 6.2 to 208 ng/g lipid weight. A slight decreasing trend of PBDE concentrations was observed in biota samples from 2005 to 2007. Log BAF (bioaccumulation factor) for PBDEs ranged from 2.4-5.6. A regression of the log BAF and log K_{OW} (the octanol-water partition coefficient) indicated a parabolic relationship for PBDEs. BDE99 does not appear to follow the same trend, which can be largely attributed to metabolism of BDE99 in organisms sampled.

Introduction

A growing environmental concern has arisen for polybrominated diphenyl ether (PBDEs) in environment and biota due to its persistence, bioaccumulation potential, and adverse effects on human health. A great number of literatures have reported the occurrence of PBDEs in biotic and abiotic matrixes [(1)]. And several studies have investigated the biomagnification of PBDEs in various food webs [(2-3)]. However, very few studies have reported the concentration of PBDEs in water thus far [(4-6)]. To better compared fish concentration data among different water body and understand the bioaccumulation behave of PBDEs in fish, it is very important to know the bioaccumulation factors (BAFs) of PBDEs in field. The Pearl River Estuary (PRE) is an important reservoir of pollutants from the Pear River Delta and serve as a source of anthropogenic pollutants for adjacent marine environment. In the present study, we collected water and aquatic organisms from the Pearl River Estuary during 2005 to 2007. The spatial and temporal distributions of PBDEs in water were examined. The BAFs of PBDEs in aquatic organisms in the PRE were calculated.

Materials and Methods

Field sampling. Water was sampled during flood seasons (May 2005, and July 2006) and dry seasons (October 2005 and 2006) at three locations along a north-south transect of the Pearl River Estuary (Fig. 1). Samples, including surface (0.5 m below air-water interface), middle (1/2 water depth), and bottom (0.5 m above surface sediment) in water columns, were collected in each station during different sampling seasons with a stainless steel submersible pump. Fish were collected using fish trawls from the marked area in the PRE (Fig. 1) during

August 2005 and August 2007. The biota species collected in the present study included sand swimming crab (*Ovalipes punctatus,* three composite samples from nine individuals), samoan crab (*scylla serrata,* two composite samples form six individuals), ark shell (*Tegillarca granosa,* three composite samples from sixty individuals), oncemelania (*Oncomelania hupensischiui,* three composite samples from thirty individuals), common mullet (*mugil cephalus,* seven individual samples), red eelgoby (*Odontamblyopus rubicundus,* three composite samples from fifteen individuals), robust tonguefish (*Cynoglossus robustus,* seventeen individual samples), slimy spinefoot (*Siganus canaliculatus,* twelve individual samples), silver sillago (*Sillago sihama,* five individual samples), pompano (*Psenopsis anomala,* six composite samples from thirty individuals), Japanese eel (*Anguilla japonica,* nineteen individual samples), flathead fish (*Platycephalus indicus,* twenty seven individual samples), large yellow croaker (*Pseudosiaena crocea,* eleven individual samples), bombay duck (*Harpodon nehereus,* six individual samples).

Extraction and cleanup. Approximately 50L of water was pumped through glass fiber filters (watermen 142 mm), then passed through a glass column filled with pre-cleaned XAD-2:XAD-4 resin. After being spiked with surrogate standards (^{13}C-PCB141 and PCB209), each resin column was eluted with 50 mL of methanol (MeOH) followed by 50 mL of dichloromethane (DCM). The resins then were extracted three times (3×100 mL) with DCM:MeOH (2:1, V:V) in an ultrasonic bath. All the eluate and extract were combined. Upon addition of 150 mL saturated NaCl solution, the combined extract was back-extracted three times, with each with 30 mL of DCM. The DCM fraction was drained through a glass column containing anhydrous $NaSO_4$ to remove any residual water. The extract was then concentrated, solvent-exchanged to hexane and further reduced to approximately 1 mL under gentle nitrogen. The concentrated extracts were fractionated on a silica/alumina column. The PBDEs were eluted with 70 mL of 50% DCM in hexane, and the extract was concentrated with a rotary evaporator to 1mL and then transported to 1.8mL vial (Wheaton, USA), and the final extract volume was reduced to 50 μL. A known amount of internal standard (BDE118, BDE128 and ^{13}C-PCB208,) was added to all extracts prior to instrumental analysis.

The procedure for biota sample extraction and cleanup was described in detail in elsewhere (Xiang et al., 2007; Wu et al., 2008). Briefly, after homogenized with ashed anhydrous sodium sulfate and spiked with surrogate standards (CDE99 and $^{13}C_{12}$- PCB141), the samples were Soxhlet extracted with hexane/acetone (1:1, v/v) for 48 h. The extracts were concentrated and an aliquot of the extract was used to lipid content determination by gravimetric method, the other aliquot was subjected to gel permeation chromatography (GPC) to remove lipids. The cleaned extract was concentrated to approximately 1 mL and further purified passing through a multilayer silica/alumina column. The extracts were concentrated, solvent exchanged to hexane, and finally concentrated to 50 μL under a gentle stream of nitrogen. A known amount of internal standard (BDE118, BDE128 and $^{13}C_{12}$- PCB 208) was added to all extracts prior to instrumental analysis.

Instrument Analysis. PBDEs were measured with a Shimadzu model 2010 gas chromatograph coupled with a model QP2010 mass spectrometer (Shimadzu, Japan) using electron capture negative ionization (ECNI) in the selective ion monitoring (SIM) mode. A DB-XLB capillary column (30 m × 0.25 mm i.d. × 0.25 μm film

thickness) was used to determinate the tri- to hepta- BDEs (BDE28, 47, 66, 100, 99, 85, 153, 154, 138, and 183). For deca-BDEs (BDE 209), a CP-Sil 13 CB capillary column (12.5 m × 0.25 mm i.d. × 0.20 μm film thickness) was used. Details of the GC temperature program as well as the procedure for qualification and quantification of PBDEs were given in published literature [7].

QA/QC. Quality assurance was done by analyses of procedural blanks, triplicate spiked blanks, and triplicate spiked matrices. For each batch of 12 samples, a procedural blank was processed. Some of the procedural blanks (n=15) contained traces of target chemicals, but the levels were close to the limit of quantification and they were subtracted from those in samples. The mean recoveries of individual congeners (BDE28, 47, 66, 100, 99, 153, 154, 138, and 183) ranged from 61% to 87% with relative standard deviations (RSDs) less than 10% in triplicate spiked blanks and from 61% to 82% with RSDs less than 15% in triplicate spiked matrices, respectively. The surrogate standard recoveries of CDE99 and $^{13}C_{12}$-PCB141 for biota samples were 83%±13% (ranged from 46%-125%) and 86%±16% (51%-118%), respectively. The recoveries of $^{13}C_{12}$- PCB141 and PCB209 for water samples were 66.3% ±26% and 98%±28%, respectively. No surrogate corrections were made to final reported concentrations.

Results and Discussion

PBDE in water. Seven congeners, BDE28, 47, 100, 99, 154, 153, 183, were found in dissolved water sample in October 2005. BDE47 and BDE99 were consistently detected in dissolved water in other three sampling seasons. The total PBDE concentrations in water in dry seasons (44-128 pg/L in October 2005 and 9.1-82 pg/L in October 2006) were higher than flood seasons (9 -18 pg/L in May 2005 and 2.5-13 pg/L in July 2006) for two years sampling period (Fig 2a, b). Theses seasonal distribution could be attributed the influence of tide and precipitation. In May of 2005 and July of 2006, the brackish water was dominant in the estuary (salinity ranged from 3-15‰. in May 2005 and ranged from 0-25%0 in July 2006). The PBDE concentrations in water were diluted by the clear sea water. But in October of 2005 and 2006, fresh water from river runoff dominated the estuary (salinity less than 3%). Additionally, the high precipitation in flood reason also diluted the PBDE levels in water. The PBDE concentrations was significantly higher in stie 1 than in site 2 and 3 in October 2005 and 2006, indicating riverine runoff was major source of PBDEs in the estuary.

There are few studies reporting the PBDE levels in water so far. Oros et al. [4] reported that the PBDE concentrations (particulate and dissolved phases) in San Franscisco Bay were in the range of 0.2~513 pg/L. BDE47, 99, and 209 were the three major detected congeners. In Lake Michigan, BDE47, 66, 99 and 100 were detected in dissolved phase with a mean value of 18 pg/L [5]. These concentrations were lower than the concentrations presented in the present study. Cetin et al. [6] reported the levels of seven PBDE congeners, namely, BDE28, 47, 99, 100, 153, 154 and 209 in Lzmir Bay, Turkey. The mean dissolved phase PBDE concentrations in summer and winter were 212 pg/L and 87 pg/L, respectively. The levels of PBDEs in the Lzmir Bay, Turkey, were comparable to those detected in the present study. Wurl et al. [8] reported the

PBDE concentrations (including BDE28, 47, 99, 100, 153, 156, 183, and 209) ranging from nondetectable to 97.8 pg/L in the seawater and from 71 to 297 pg/L in the sea-surface microlayer in Hong Kong. No BDE209 was detected in their study. The range of PBDE concentrations in the Hong Kong coastal area was similar to our study.

PBDE in biota. Of the 10 PBDE congeners measured, BDE28, 47, 66, 100, 99, 154, and 153 were detected in more than 70% of samples but BDE138, 183, and 209 were detected in less than 60% of samples (59%, 35%, and 18%, respectively). Therefore, data for ∑PBDEs only contained the congeners of BDE28, 47, 66, 100, 99, 154, and 153. Bombay duck, ark shell, and large yellow croaker had relative low PBDE concentrations with median of 9.8, 13, and 13 ng/g lipid weight (lw), respectively. Sand swimming crab, samoan crab, oncomelania, common mullet, red eelgoby, and silver sillago had similar PBDE levels with median ranging from 17 to 21 ng/g lw, which were lower than those (median ranged from 29 to 32 ng/g lw) in robust tonguefish, slimy spinefoot and Japanese eel. The highest concentration was found in flathead fish with a median of 59 ng/g lw. The levels of PBDEs in the present study were significant lower than those in biota samples collected in the same area in 2004 (median ranged from 67 to 194 ng/g lw) [9], indicating a decrease trend for PBDEs level in biota in the study area. In the present study, samples of robust tonguefish, Japanese eel, and flathead fish were annually collected in 2005, 2006 and 2007. The concentrations of ∑PBDEs in the three years were illustrated in Fig. 3. It was clear that a decreasing trend of ∑PBDEs in biota was observed although no statistical significance was obtained, which confirmed the above conclusion.

BDE47 was the most abundant congener in aquatic species and was usually chosen as a representative of PBDE contaminants. In the present study, the concentrations of BDE47 in biota ranged from 2.3 to 38 ng/g lw, which were close to the concentrations in fishes from Lake Winnipeg, Canada (1.8-84 ng/g lw) [10], from southern Greenland (7.9-41 ng/g lw) [11], and from Canadian Arctic (2.9-26 ng/g lw). The concentrations of BDE47 in the present study were much lower than those reported concentrations in Laizhou Bay (30-240 ng/g lw) [12], and coastal British Columbia (6.1-160 ng/g lw) [13] but higher than those from Vietnam Can Tho (0.4-0.7 ng/g lw) [14], and Bohai Bay (0.03-3.8 ng/g lw) [15].

Bioaccumulation factors. Bioaccumulation factors (BAFs) are defined as the ratio of fish tissue concentration to dissolved water concentration expressed in equivalent units. BAF= pg/kg wet weight/ pg/L The concentration of PBDEs in water used to calculate the ratio was the mean concentration in four sampling reasons. Log BAF of PBDE congener ranged from 2.4-5.6 for all organisms, which is similar to those (2.9-5.3) in aquatic species from a pond in an e-waste recycling site in South China [16], and those (2.2-6.2) in river received municipal sewage treatment plant effluent in north China [3]. However, these values were lower than those (6.7-7.5) for lake trout from Lake Michigan [5] and were higher than those (2.1-4.5) for fish in Winnipeg Lake [10].

The log BAF was plotted versus log K_{OW} for PBDEs in all the aquatic species in Fig 4. Apparently, a

parabolic relationship between log BAF and log K_{OW} was found. The highest BAF was found in BDE100, which have a log K_{OW} of 7.2. This trend has been previously reported and explained for PCBs in others studies [3, 17]. This result suggested that PBDEs might exhibit bioaccumulation behavior similar to that of PCBs. BDE99 were depressed from the general trend in all aquatic species, which further supports the conclusion that BDE99 undergoes debromination in fish.

Acknowledgments

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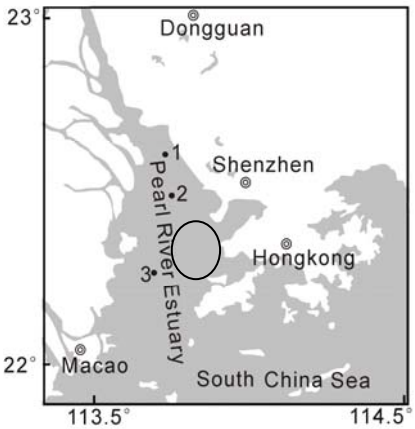

Fig 1 Map of the sampling location for water and organisms from PRE

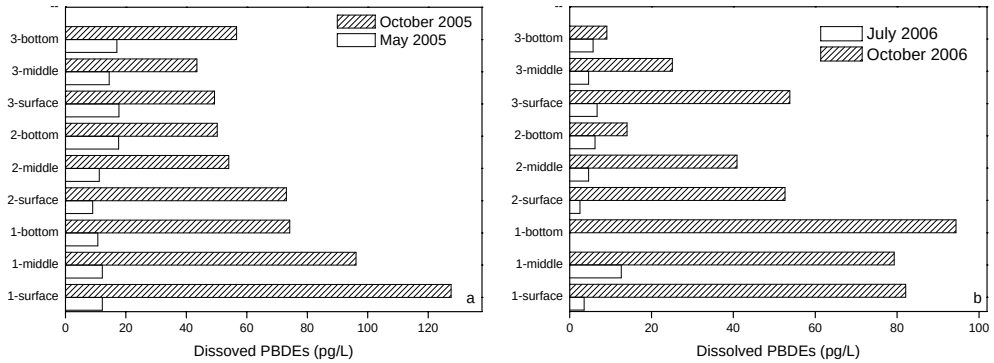

Fig 2 spatial and temporal distribution of PBDEs in water.

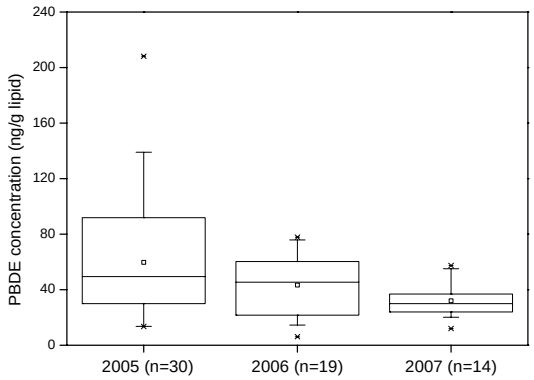

Fig 3 Box plot concentrations of ∑PBDE in biota from the Pearl River Estuary among 2005 and 2007.

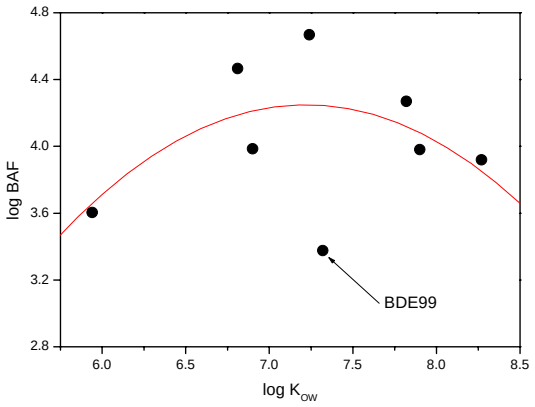

Fig 4 log BAF vs log KOW for PBDE congeners.