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Polybrominated diphenyl ethers in fish and sediment from river polluted by electronic waste

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Abstract

The present study investigated contamination of polybrominated diphenyl ethers (PBDEs) in sediment and fish samples collected from rivers in Guiyu, China where electronic waste (e-waste) is recycled and disposed. PBDE congeners with mono-to hepta-brominated and deca-brominated substitutions were detected using $^{13}C_{12}$ isotope dilution GC/MS/MS and GC/MS methods, respectively. The total PBDE concentrations ranged from 4434 to 16088 ng/g (dry weight) in Nanyang River bank sediment, from 55 to 445 ng/g in Nanyang River bottom sediment and 51.3 to 365 ng/g in Lianjiang River bottom sediment in Guiyu compared with those from 16.1 to 21.4 ng/g in wastewater discharged from a vehicle repairing workshop in Lo Uk Tsuen in Hong Kong. No PBDE congeners were detected in bottom sediment and fish from Mai Po Marshes in Hong Kong.

The mean concentrations of total PBDEs in mixed muscles of tilapia (*Oreochromis* spp) from Lianjiang River were 115 ng/g wet weight (ww) and from wastewater in Hong Kong were 4.1 ng/g ww. Highest mean PBDE concentration was obtained in liver (2687 ng/g ww), followed by abdomen muscle (1088 ng/g ww) of bighead carp (*Aristichthys nobilis*) collected from Nanyang River. A significant correlation of concentration of each PBDE congener between sediment and muscle from Guiyu was observed. The present results of total PBDEs in sediment and fish were 10 and 1000 times higher than other studies. Open burning and dumping of e-waste are the major causes of PBDE contamination.

Keywords: PBDEs; E-waste; Sediment; Fish; Bioaccumulation; Correlation

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are one of the brominated flame retardants (BFRs) used to protect potentially flammable organic materials by increasing the resistance to ignition and delaying the spread of fire. They are widely applied for textile, building material, motor vehicle, electrical and electronic equipment, and commercial products which almost doubled in the last decade (Alaee et al., 2003). PBDEs can be dissolved in materials and then leached into the environment and entered biota (Strandberg et al., 2001). PBDEs are similar to polychlorinated biphenyls (PCBs) in structure and characteristics such as hydrophobic and semi-volatile and/or fairly nonvolatile (Palm et al., 2002). The higher brominated substitutes are less mobile in the environment, possibly because of their low volatility, water solubility and strong adsorption on solid samples (Watanabe and Sakai, 2003).

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PBDEs were first detected in the sludge samples collected from plants that manufactured polybrominated compounds in the US (de Carlo and Ann, 1979) and in fish caught from river nearby textile industries in Sweden (Andersson and Blomkvist, 1981). The PBDEs have been found at relatively high concentrations in abiotic environment including sediment, sewage sludge (Nylund et al., 1992; Stapleton et al., 2005) and biota (Law et al., 2006) such as farmed and wild fish (Hites et al., 2004; Montory and Barra, 2006) and marine fish (Johnson-Restrepo et al., 2005). They have become global contaminants demonstrating by their presence in tissue samples of fish-eating birds and marine mammals collected from the Baltic Sea and Arctic Ocean in 1987 (Jansson et al., 1987). They were also detected in the muscle of skipjack tuna (*Katsuwonus pelamis*) collected from offshore waters of various regions in the world, indicating widespread contamination by these compounds in the marine environment (Ueno et al., 2004). These evidences proved that PBDEs are bioaccumulated and biomagnifed in marine ecosystems (Boon et al., 2002).

Tetra- and penta-BDEs are more persistent, lipophilic and bioaccumulated than octa- or deca-BDEs (de Boer et al., 2000). It has been shown that the level of the commercial penta-BDEs product increased with the age of teleost (carp) (Hardy, 2000). PBDEs are persistent with an environmental dispersion pattern similar to PCBs (de Wit, 2002) and are potential endocrine disrupting compounds (Hooper and McDonald, 2000). The biomagnification rates of PBDEs are higher than that of PCBs (Burreau et al., 1999). Decrease of free thyroxin hormone (T4) has been observed in animals after exposure to PBDEs (de Boer et al., 2000). It is suspected that these toxic chemicals are transferred to sediment and water, taken up by aquatic organisms, and eventually impose adverse effects on human health. The most probable route for exposure of human beings to PBDEs, especially lower brominated congeners is through diet such as freshwater fish (Schecter et al., 2006).

Based on recent risk assessments, Penta- and Octa-BDEs products have been banned within the EU in 2004. However, there are no restrictions on the use of Deca-BDEs. The heavy application of BDE-209 in electronic equipment results from slow leaching from these products into the environment where it can be transported in the atmosphere (Strandberg et al., 2001), leading to its extensive presence throughout the world. BDE-209 was detected with maximum concentration of 320 ng/g but tri-BDEs to hepta-BDEs ranged from 0.2 to 19 ng/g in the Western Scheldt Estuary that close to PBDEs factories (Voorspoels et al., 2004). PBDE concentrations were low and even below detection limits in remote locations samples but high in the sheltered waters of Victoria Harbour. Only trace amounts of BDE-209 were detected in the sediments (1.7 to 53.6 ng/g) and mussel tissues (27.0 to 83.7 ng/g dw) from Hong Kong marine waters (Kajiwara et al., 2006; Liu et al., 2005; Wurl et al., 2006). It is suggested the relatively low levels of PBDEs in marine waters may originate from the disposal of electronic waste in southern China, as well as local untreated wastewater discharge (Wurl et al., 2006). Congener composition was also dominated by BDE-209 (72.6–99.7% of total PBDEs) ranged from 0.4 to 7340 ng/g, with minor contributions come from penta- and octa-BDEs in sediments of the Pearl River Delta (PRD) (Mai et al., 2005).

Electronic waste (e-waste) includes end-of-life electronic products such as computers, printers, photocopy machines and television sets. Obsolete electronic products are exported to developing countries for recycling due to there lower labor cost and less stringent environmental regulations in the receiving country (Puckett et al., 2002). High concentrations of PBDEs have been found in individuals working at a computer disassembly facility in Sweden (Julander et al., 2005).

However, uncontrolled dismantling, acid treatment, and open burning resulted in adverse environmental effects according to our previous survey at Guiyu, southwest Guangdong Province, PR China (Leung et al., 2006). Approximately 145 million electronic devices (including television sets, computers, electric fans, etc.) were scrapped in 2002 (Terazono et al., 2006). Recently, an increasing amount of e-waste is stored in the New Territories of Hong Kong, due to the fact that the mainland China has tightened up her regulations on e-waste importation. Brominated flame retardants (BFRs) were detected in several e-waste recycling workshops in the New Territories (Planet, 2005).

Our previous studies indicated that soils and sediments were highly contaminated by different recycling activities of e-waste in Guiyu of Guangdong Province (Wang et al., 2005) and Taizhou of Zhejiang Province (Cai and Jiang, 2006). However, there is a lack of information on PBDEs in fish collected from river polluted by dumping of e-waste.

With the above background, the major objective of the present study is to identify the concentrations and congener patterns of PBDEs in river sediment and fish from the e-waste site at Guiyu and compare with river sediment and fish collected from a site (Lo Uk Tsuen, Hong Kong) receiving discharge from a motor repairing workshop. Samples from a remote site at Mai

Po Marshes, New Territories, Hong Kong were also collected as control for comparison. It is also hoped to see if there are specific congener patterns indicated of specific emission sources, so that we may use as a kind of fingerprint.

2. Materials and methods

2.1. Chemicals and reagents

Dichloromethane (DCM), hexane and acetone were purchased from Tedia Company Inc. (Fairfield, OH, USA) and nonane from Fluka (Milwaukee, USA) at pesticide grade. Granular anhydrous sodium sulfate were obtained from Tedia (Fairfield, USA), silica gel 60 (0.063–0.200 mm) from Merck (Whitehouse Station, USA), acid alumina (Brockmann I, Standard Grade, ~150 mesh) from Aldrich Chemical Co. (Milwaukee, USA), copper powder from UniChem (Surrey, UK) and concentrated sulfuric acid from BDH Laboratory Supplies (Dorset, UK) at analytical grade.

Standard solutions of PBDEs were purchased from Wellington Laboratories (Ontario, Canada) in 2004. A calibration solution BDE-CVS-E (5 ampoules in 1 kit) contained main PBDE congeners (BDE-3, 7, 15, 17, 28, 47, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183 and 209), and a native PBDE standard mix containing BDE-MXD (BDE-17, 47, 66, 100, 153, 183 and 209) and $^{13}C_{12}$-labeled PBDE mix (MBDE-MXC) ($^{13}C_{12}$-labeled BDE-15, 28, 47, 99, 153, 154 and 183) and $^{13}C_{12}$-labeled BDE-209 were used to optimize extraction and cleanup procedure for recovery.

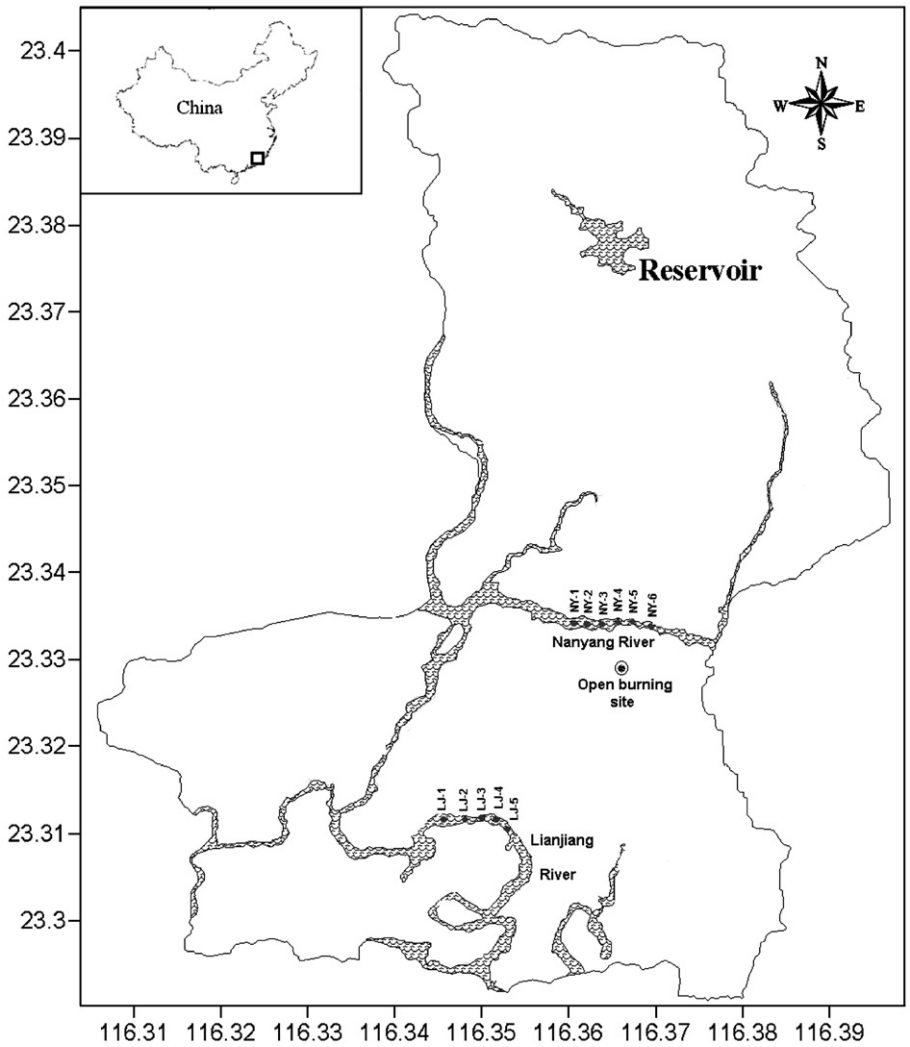

Fig. 1. Sampling locations in Guiyu of Guangdong Province and Hong Kong, China. (The distance from Guiyu to Hong Kong is about 400 km).

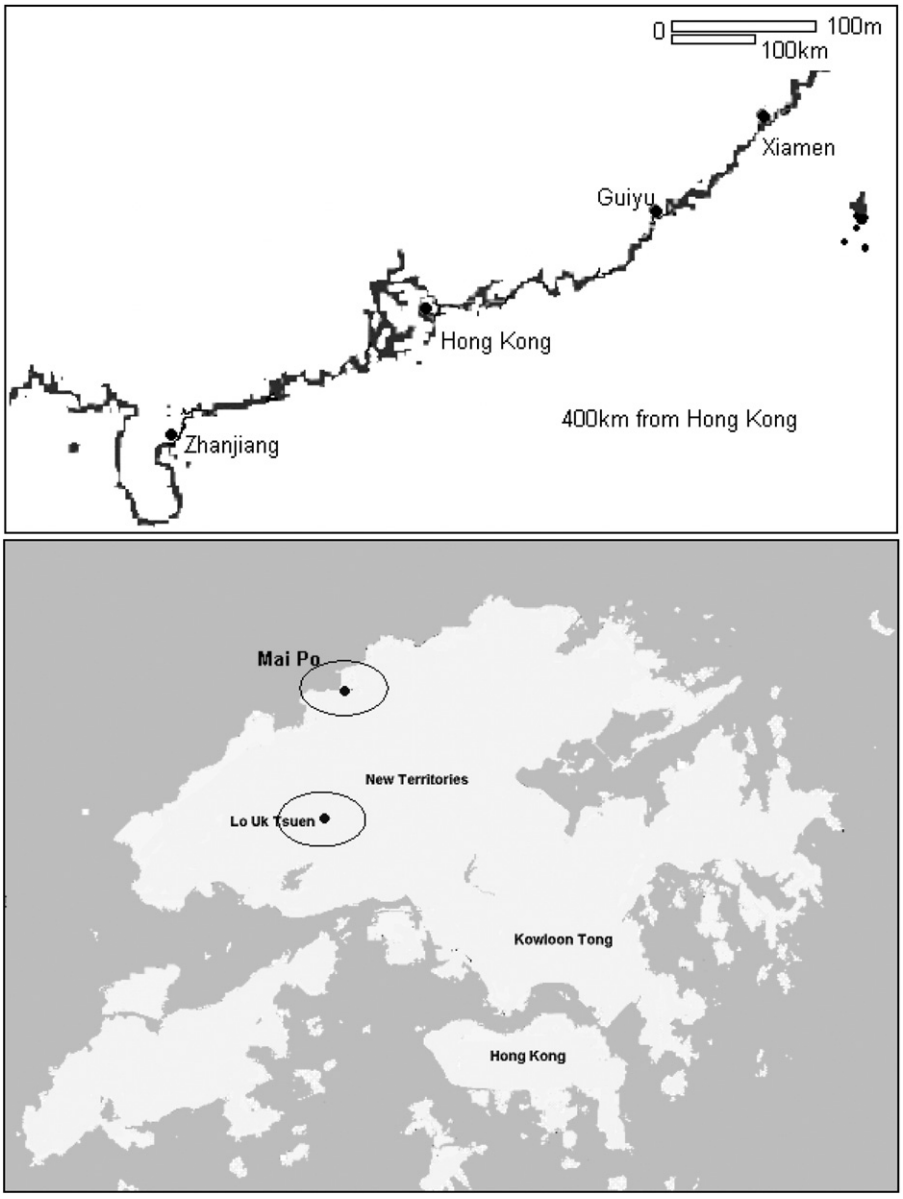

Fig. 1 (*continued*).

2.2. Sample collection and treatment

During December 2004, surface sediments (0–10 cm) (NY-I) were collected: from 6 locations along the bank of Nanyang River (N: 23.3215; E: 116.369), in which processed e-waste and burned ashes were dumped. At same locations, bottom sediments (NY-II) (depth: 0–30 cm), near the largest open burning site where printed circuit boards, chipping and plastics were burned with unpleasant odor were also collected. Bottom sediments (depth: 0–30 cm) were also collected from 5 locations of Lianjiang River (LJ) (N: 23.3121; E: 116.352) located next to a residential area in town. Bottom sediments (depth: 0–10 cm) were also collected from the river receiving wastewater in Lo Uk Tsuen (LUT) of Hong Kong (N: 22.25; E: 113.967) discharged from a motor vehicle repairing workshop. Sediments (depth: 0–30 cm) from the fish ponds in Mai Po Marshes (MP) (N: 22.467; E: 114.033) in Hong Kong were also collected and served as a control (Fig. 1). The samples were collected using a Wildco sediment grab (Wildco Wildlife Supply, Saginaw, Michgan) and wrapped with clean aluminum foil and placed in hexane-washed containers, with ice bar (at 4 °C) and

transported to the laboratory immediately, and stored at −20 °C.

Six bighead carps (*Aristichthys nobilis*) from Nanyang River, eighteen tilapias (Oreochromis spp) from Lianjiang River and nine tilapias from the river receiving waste water in Lo Uk Tsuen and nine tilapias from Mai Po Marshes were collected using a net. All fish were wrapped in aluminum foil and transported to the laboratory at 4 °C. Fish samples were thawed and their weights and lengths were measured. Tilapias were grouped randomly into three composite samples consisting of three fishes each with similar length. Due to their smaller size (length: 10–12 cm), fish samples from Mai Po should were grinded and mixed for analysis. Nine tilapias from LJ (length: 22.5–27 cm) and six bighead carps from NY (length: 37–43 cm) were divided into abdomen, back and tail muscles. In addition, the liver of bighead carps was also separated. Divided muscles and liver were wrapped in aluminum foil and stored at −20 °C.

2.3. Extraction and cleanup

The sediment samples from each sampling site were mixed together and freeze-dried, grinded and passed through a 1 mm sieve pore. About 10 g of the dried sediment was mixed with 4 g of anhydrous sodium sulfate (cleaned with DCM and activated at 140 °C for 24 h), 5 g of granular copper (used to remove elemental sulfur) with 10–50 ng of MBDE-MXC ($^{13}C_{12}$-labeled BDE-15, 28, 47, 99, 153, 154 and 183) and $^{13}C_{12}$-labeled BDE-209 prior to the extraction with 80 mL of acetone-hexane (1:1, v:v) for 16 h at 80 °C.

The extractable lipids were then determined gravimetrically (Hara and Radin, 1978). After freeze-dried for 10 days, fish muscle was grinded and mixed thoroughly by an electric blender. About 5 g of dried fish muscle±or 1 g of bighead liver) was also mixed with 10 ng of MBDE-MXC and 4 g of anhydrous sodium sulfate, before extracting with 80 mL of DCM/acetone (1:1, v:v) for 12 h in Soxhlet extraction system.

The sediment or muscle extract was concentrated with a rotary evaporator and then transferred to a glass bottle with 6 mL hexane. They were treated with concentrated sulfuric acid to remove the sulfuric compound (in sediment sample) and the bulk of lipids (in fish muscle and liver), followed by an additional cleanup step to remove other interferences. Further cleanup was done on a column containing 2 g anhydrous sodium sulfate, 1 g of silica gel impregnated with sulfuric acid (44%), 3 g 30% acid silica gel and 1 g active silica gel from top to bottom. N-hexane (30 mL) was used for the elution. The eluted solution was loaded on to a column containing 2 g anhydrous sodium sulfate and 4 g acid alumina. The column was eluted with 30 mL n-hexane/DCM (7:3, v:v) that was collected and concentrated under gentle nitrogen evaporation apparatus at room temperature. The sample was reconstituted in 50 μL nonane containing $^{13}C_{12}$-BDE-139 at 100 pg/μL.

2.4. GC/MS/MS and GC/MS analysis

GC/ion trap MS analysis was performed on a Trace GC/PolarisQ ion trap mass spectrometer (Thermo Quest, Austin, TX, USA). A DB-5 ms column (30 m * 0.25 mm I.D., 0.25 μm film thickness) was used for the determination of congeners from mono- to hepta-BDEs. The temperature program was from 110 °C (held for 1 min) to 180 °C (held for 1 min) at 8 °C/min, then from 180 to 240 °C (held for 5 min) at 2 °C/min, and then from 240 to 265 °C (held for 6 min) at 2 °C/min. The GC injector temperature was maintained at 290 °C. The temperatures of the MS ion source and transfer line were kept at 250 and 300 °C, respectively. Sample extract or standard solution (1 μL) was injected with a solvent delay set at 6 min. The mass spectrometer was operated with electron impact ionization (EI) mode at source temperature of 250 °C and electron energy of 70 eV. Under the EI-MS conditions, the molecular ions ($[M]^+$or $[M+2]^+$) and fragment ions resulting from the loss of Br_2 (i.e., $[M\text{-}Br_2+2]^+$or $[M\text{-}Br_2+4]^+$) were selected as the precursor ions for tandem mass spectrometric analysis. The quantitative ions were selected based on the criteria of peak intensity and ion specificity as well as potential interference from other compounds. The important instrumental parameters, i.e. the "*q*" value, resonant excitation voltage (REV), excitation time (ET) and isolation time (IT) (Luo et al., in press) were optimized in order to obtain maximum selectivity and sensitivity.

GC/MS analysis of BDE-209 was performed on Agilent 5975 GC/MSD with a DB-5 ms (15 m * 0.25 mm I.D., 0.10 μm film thickness), with the temperature program from 150 °C (held for 1 min) to 300 °C (held for 18 min) at 30 °C/min. MS detector condition was performed by EI (70 eV) and selected ion monitoring (SIM) of high abundance (m/z 799.3).

2.5. Quality assurance and quality control

The limits of detections (LOD) were 0.01–0.1 ng/g for mono-to hepta-BDEs and 1 ng/g for deca-BDE. Instrument calibration was performed using PBDEs standard solution over the concentration range from 1 to 1000 pg/μL at five concentration levels. Control sediment and tilapia samples were collected from Mai Po Marshes (a remote nature reserve). A native PBDE standard (BDE-MXD)

was added to control samples prior to extraction. The recoveries of 87 to 103% control samples (sediment and fish) were obtained. Mass labeled (MBDE-MXC: eight congeners of $^{13}C_{12}$-labeled BDEs at 10 ng and $^{13}C_{12}$-labeled BDE-209 at 20 ng) were used as internal standards for PBDEs taken through all phases of the analytical procedure, and $^{13}C_{12}$-BDE-139 with the retention time closest to a target analyte was used as the internal standard. The recovery rates $^{13}C_{12}$-labeled-PBDEs spiked to sediment and fish samples ranged from 78 to 113% and 88 to 108%, respectively.

2.6. Statistical analysis

Statistical analyses were performed using Microsoft Excel XP and SPSS 13.0 statistical software. Values were considered significantly different when $p<0.05$. Differences between fish part were tested using single factor ANOVA. As significant relationships of PBDE concentrations were observed between lipid contents and concentrations in fish muscle and between sediment and fish muscle, data were analyzed using ANOVA.

3. Results

3.1. PBDE concentrations and congener patterns in sediment

Table 1 lists the mean concentrations (ng/g dry weight) of total PBDEs (from mono- to hepta-BDEs and deca-BDE, with 14 main congeners) in sediments collected from bank sediment in Nanyang River (NY-I), bottom sediments from Nanyang River (NY-II) and Lianjiang River (LJ) in Guiyu and wastewater from Lo Uk Tsuen (LUT) in Hong Kong. The total PBDE concentrations in sediments, ranged from 4434 to 16,088 ng/g in NY-I, 55 to 445 ng/g in NY-II, 51.3 to 365 ng/g in LJ and 16.1 to 21.4 ng/g in LUT. PBDE congeners were not detected in sediments from MP. The descending order of PBDEs was: NY-II > LJ > LUT > MP. The river bank sediment at NY-I contained very high concentrations of BDE-47, -99, -153, -100 and-183, and moderate concentrations of these congeners were observed in bottom sediments of both NY-II and LJ from Guiyu. The discharge of vehicle repairing workshop (LUT) contained comparatively low levels of all these congeners.

Different congener pattern profiles were observed in sediment collected from each sampling site (Fig. 2), with BDE-47 the predominant congener, followed by BDE-99 and-153 in NY-I and NY-II, but-209 had a major contribution in NY-II. BDE-47, 99, 183 and 209 were dominant congeners obtained in LJ, while BDE-209, 183, 154 and 99 were dominant congeners in LUT.

3.2. PBDE concentrations and congener patterns in fish

Table 2 shows the sum of PBDEs (11 main PBDE congeners except BDE-3, -7 and -77 with no detectable concentration in fish samples). The results of mixed muscle of tilapia were compared among MP, LUT and

Table 1
Individual and total PBDE concentration in sediments from Guiyu and Hong Kong (ng/g dry weight)

Congener	Hong Kong			Guiyu					
	MP	LUT (bottom)		LJ (bottom)		NY-I (bank)		NY-II (bottom)	
	Mean	Mean±std	Range	Mean±std	Range	Mean±std	Range	Mean±std	Range
BDE-3	nd	nd	nd	0.5±0.5^{b}	0–1.1	9.3±6.4^{a}	1.4–17	nd	0–0.1
BDE-7	nd	nd^{c}	nd	0.2±0.3^{b}	0–0.8	10.4±4.5^{a}	2.9–14.3	0.1±0.1^{b}	0–0.2
BDE-15	nd	nd^{c}	0.02–0.2	0.7±0.5^{b}	0.2–1.4	23±7.0^{a}	9.2–27.1	0.6±0.3^{b}	0.2–1.2
BDE-17	nd	0.1^{b}	0.01–0.1	0.9±0.9^{b}	0.2–2.3	48±14.7^{a}	24.0–70.2	0.4±0.3^{b}	0.1–0.9
BDE-28	nd	0.1±0.2^{c}	0.03–0.4	2.8±2.8^{b}	0.4–7.5	232±148^{a}	20.7–443	2.4±1.5^{b}	0.8–4.8
BDE-47	nd	0.6±0.2	0.8–1.2	40±53^{b}	4.9–133	3054±1651^{a}	1219–5763	73.4±51.1^{b}	15.2–131
BDE-66	nd	1.2±0.5^{b}	1.1–2.0	11±15^{b}	1.6–38	158±118^{a}	41.3–334	4.0±3.4^{b}	0.5–9.6
BDE-77	nd	0.9±0.3^{b}	0–0.6	0.8±1.5^{b}	0–3.5	90±72.5^{a}	8.5–186	3.6±2.1^{b}	1.2–5.7
BDE-100	nd	0.3±0.1^{c}	0.1–0.2	1.3±1.6^{b}	0.2–4.1	391±181^{a}	240–629	7.0±5.5^{b}	1.4–12.8
BDE-99	nd	1.4±0.4^{c}	2.1–2.9	33±40^{b}	4.5–103	2827±1682^{a}	1297–5249	65.5±50.2^{b}	9.7–119
BDE-154	nd	1.5±0.1^{c}	0.3–0.5	4.0±1.4^{b}	2.1–5.5	402±163^{a}	204–610	6.2±7.4^{b}	0.5–18.3
BDE-153	nd	0.8±0.4^{d}	0.7–1.5	11±7.4^{c}	3.4–21	1834±650^{a}	1056–2657	24.8±39.9^{b}	1.7–104
BDE-183	nd	2.3±1.2^{c}	2.2–4.6	20±23^{b}	3.6–59	241±101^{a}	113–345	6.4±6.3^{c}	0.1–14
BDE-209	nd	6.0±0.4^{b}	8.1–8.8	30±20^{a}	15–57	35.9±18.3^{a}	16.9–62.2	31.1±18.3^{a}	13.9–53.9
Total PBDEs	nd	13.9±2.8^{c}	16.1–21.4	156±131^{b}	52–365	9357±4545^{a}	4434–16088	225±162^{b}	55–445

nd: not detected; MP: Mai Po Marshes (control site); LUT: wastewater discharge from vehicle repairing workshop in Lo Uk Tsuen; LJ: Lianjiang River near living location; NY: Nanyang River near to e-waste open burning and dumping site. The different letters in the same row contain mean±standard deviations. A significant difference is at $p<0.05$ according to Duncan's Multiple Range Test.

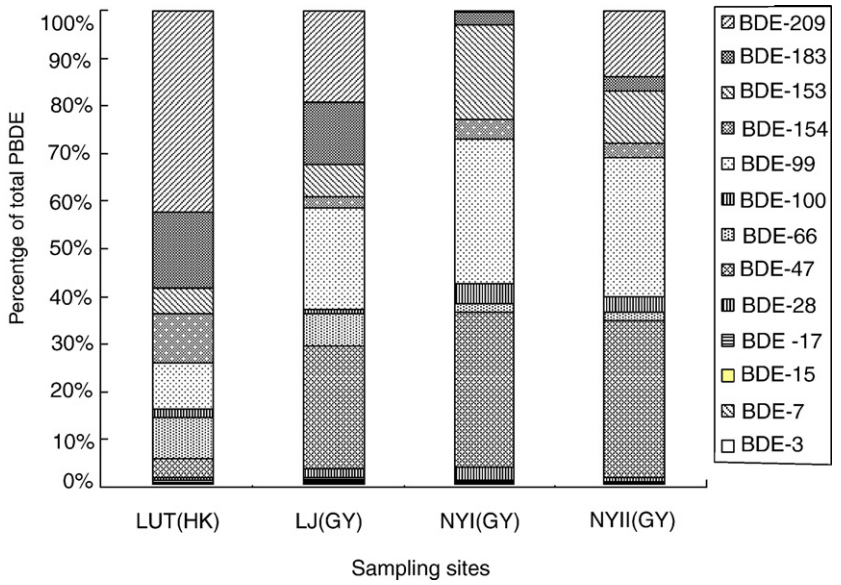

Fig. 2. Percentage contributions of total PBDE congeners detected in bottom sediments of LUT (HK) (Lo Uk Tsuen) from Hong Kong, LJ (Lianjiang River)and NY-II (Nanyang River) and bank sediment of NY-I (Nanyang River) from Guiyu (GY).

LJ. No PBDE congeners were detected in MP. Higher concentrations of all congeners were observed in LJ (115 ng/g ww) than LUT (4.1 ng/g ww).

Individual PBDE congener concentrations in different parts of tilapia and bighead carp from Guiyu were different possibly due to the difference of their lipid content. The mean concentration of total PBDEs in tilapia was 483 ng/g ww in abdomen muscle (lipid content: 9.2±2.1%), 67.8 ng/g ww (lipid content: 3.5±0.8%) and 84.8 ng/g ww (lipid content: 4.1±1.0%) in back and tail muscle, respectively. The mean concentration of total PBDEs of bighead carp was 1088 ng/g ww (lipid content: 16.2±2.1%) in abdomen muscles, 35.1 ng/g ww (8.9±1.2%) and 41.8 ng/g ww (9.4±1.4%) in back and tail muscles, respectively. Higher levels of PBDEs were revealed in liver (2687 ng/g ww) than in muscle of

Table 2
Individual congener and total concentrations of PBDE in different parts of fish from Guiyu and Hong Kong. (ng/g wet weight)

Congeners	Tilapia (n=9)			Tilapia (n=9)			Bighead carp (n=6)			
	MP	LUT	LJ	LJ			NY			
	Mixed muscle	Mixed muscle	Mixed muscle	Abdomen muscle	Back muscle	Tail muscle	Abdomen muscle	Back muscles	Tail muscles	Liver
BDE-15	nd	0.02±0.01^{b}	3.9±1.8^{a}	9.8±10.8^{a}	1.2±1.1^{b}	1.8±1.8^{b}	95.4±6.2^{c}	4.2±4.1^{c}	4.3±4.1^{c}	213±28.3^{a}
BDE-17	nd	nd^{b}	0.2±0.1^{a}	9.6±9.2^{a}	5.8±5.2^{b}	1.4±1.5^{b}	23.7±20.4^{b}	1.4±0.2^{b}	2.9±0.5^{c}	73.3±39.6^{a}
BDE-28	nd	0.09±0.03^{b}	13.4±6.0^{a}	42.8±41.4^{a}	6.8±5.8^{c}	7.4±6.6^{c}	282±22.1^{c}	8.2±1.1^{c}	9.6±2.1^{c}	626±411^{a}
BDE-47	nd	2.35±0.07^{b}	69±30.1^{a}	333±236^{a}	45.8±34.4^{b}	60.2±46.6^{b}	630±46.2^{b}	19.3±1.2^{c}	23.4±2.2^{c}	1644±747^{a}
BDE-66	nd	0.19±0.03^{b}	6.9±3.1^{a}	24.4±23.3^{a}	1^{b}	3±1.6^{b}	nd	nd	nd	nd
BDE-100	nd	0.24±0.08^{b}	3.6±1.5^{a}	1.2±0.5^{a}	1±1.2^{a}	1^{a}	22.4±17.2^{b}	0.7±0.6^{c}	0.4±0.2^{c}	48.5±21.9^{a}
BDE-99	nd	0.17±0.08^{b}	4.0±2.8^{a}	10.6±11.2^{a}	4.4±3.8^{b}	1.4±1.5^{b}	8.0±5.7^{b}	0.3±0.1^{c}	0.2±0.1^{c}	11.4±7.1^{a}
BDE-154	nd	0.51±0.16^{b}	8.8±6.5^{a}	36.4±27.1^{a}	1.8±1.3^{c}	6±4.9^{b}	9.5±4.9^{b}	0.7±0.3^{c}	0.5±0.1^{c}	26.5±12.1^{a}
BDE-153	nd	0.24±0.10^{b}	5.3±3.0^{a}	15.2±11.3^{a}	nd^{c}	2.6±2.1^{b}	16.5±9.2^{b}	0.3±0.1^{c}	0.5±0.2^{c}	43.3±7.1^{a}
BDE-183	nd	0.03±0.01^{a}	0.01±0.01^{a}	0.1±0.2^{a}	nd^{b}	nd^{b}	0.23±0.18	nd	nd	nd
BDE-209	nd	nd	nd	0.01±0.01^{a}	nd^{b}	nd^{b}	nd	nd	nd	nd
Total PBDEs	nd	3.84±0.57^{b}	115±54.9^{a}	483±371^{a}	67.8±52.8^{b}	84.8±66.6^{b}	1088±132^{b}	35.1±7.7^{c}	41.8±9.5^{c}	2687±1274^{a}
Lipid%	8.2±1.5%	7.9±3.2%	7.3±1.5%	9.2±2.1%	3.2±0.8%	4.1±1.8%	16.2±2.1%	8.9±1.2%	9.4±1.4%	20.2±1.5%

nd: not detected; MP: Mai Po Marshes (control site); LUT: wastewater discharge from vehicle repairing workshop in Lo Uk Tsuen; LJ: Lianjiang River near living location; NY: Nanyang River near to e-waste open burning and dumping site. The different letters in the same rows (of the mean±standard deviation) of same column indicate a significant difference at $p<0.05$ level according to Duncan's Multiple Range Test.

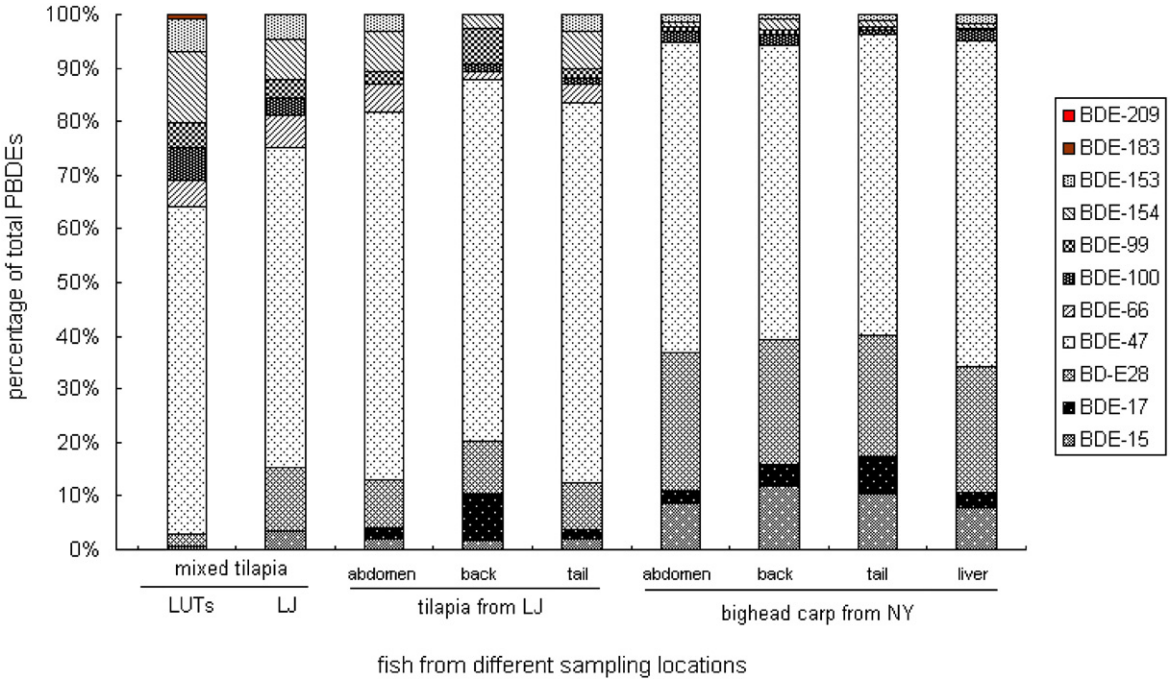

Fig. 3. Percentage contributions of total PBDEs congeners are detected in tilapia and bighead carp (MP:Mai Po Mashes; LUT: Lo Uk Tsuen in Hong Kong; LJ: Lianjiang River and NY: Nanyang River from Guiyu).

bighead (Table 2). Liver contained the highest concentrations of PBDEs, followed by abdomen muscle whereas similar concentrations were noted in tail and back muscle.

PBDE concentrations in abdomen muscles were significantly higher ($p<0.05$) than those in back, tail and mixed muscles of tilapia and bighead carp. No significant difference ($p>0.05$) was observed between back and tail muscles for PBDEs in tilapia and bighead carp, except BDE-7 and-100 (at lower concentrations) in tilapia.

Congener pattern distributions in tilapias and bighead carps are shown in Fig. 3. The descending trend of congeners with tetra-BDEs>hexa-BDEs>penta-BDEs was observed in tilapias from LJ and LUT. BDE-47 was the predominant congener observed followed by BD-154 and -153 in tilapia from LJ; and BDE-28 and BDE-66 in bighead carp from NY. However, BDE-154, 153, 100 and 99 were very low. In addition, BDE-28 contributed to the major portion (20.3%) of total PBDEs in muscles of bighead carp.

4. Discussion

The mean concentrations of total PBDEs (156 to 9357 ng/g) in sediments in Guiyu are much higher than those in LUT and other studies (Table 3), almost 10 to 1000 times. In general, PBDE levels in river and marine sediments varied from nanograms per gram to micrograms per gram dry weight, depending on the sampling locations (de Wit, 2002). Heavily industrialized and populated areas are generally more contaminated. The most obvious sources are effluents from factories producing BFRs, poly urethane foam (PUF), textile and plastic products such as electronic appliance. In addition, PBDEs in bottom sediment from NY-II (55 to 445 ng/g) and LJ (52 to 365 ng/g) in Guiyu are within the same order of magnitude of some polluted sites reported elsewhere. However, some sampling locations of Nanyang River (4434 to 16,088 ng/g) in Guiyu are seriously polluted by e-waste materials due to open burning and uncontrolled dumping.

Different concentrations and congener pattern profiles of sediments are found in each sampling site (Fig. 2) which reflected input from varying sources according to different locations and types of e-waste materials involved. The mean concentrations of BDE-209 in different sites were similar, with 36 ng/g in NY-I, 31 ng/g in NY-II and 30 ng/g in LJ. A lower concentration (6 ng/g) in LUT while it was not detected in MP. The total PBDE concentrations (except BDE-209) in sediments from NY-I are 100-1000 times higher than that from NY-II and LJ, due to residues of burned e-waste materials and plastic chips disposed along the bank of Nanyang River. BDE-47, 99, 153 and 183 were dominant congeners in NY-I (bank sediment) and NY-II

Table 3
Compared PBDE concentrations in sediment samples from Guiyu and Hong Kong with other studies at highest concentration levels (ng/g dry weight)

Sampling locations	Highest PBDE concentrations (ng/g)	Reference
River sediment in Pearl River Delta	13.03	Zheng et al. (2004)
River sediment in industrial areas of Portugal	21	Lacorte et al. (2003)
Contaminated river sediment in Japan	70	Darnerud et al. (2001)
Sewage sludge from Bjergmarken sewage treatment plants (STP) in Roskilde, Denmark	200	Christensen et al. (2003)
Downstream sediment of an area with textile industries	120	Sellström et al. (1998)
Downstream sediment of a foam manufacturing plant	1400	Alaee et al. (2003)
Sediment from wastewater discharge from the vehicle repairing workshop in Lo Uk Tsuen, Hong Kong	21.4	The present study
Bottom sediment Lianjiang River in Guiyu	365	The present study
Bottom sediment from Nanyang River in Guiyu	445	The present study
Bank sediment from Nanyang River in Guiyu	16088	The present study

(bottom sediment) were be possibly due to the contamination by the commercial Penta-BDEs and Octa-BDEs products used in electronic equipment.

BDE-47 concentration ranged from 34 to 41% of total PBDEs (from tri- to hexa-BDEs) in NY-I, NY-II and LJ from Guiyu which was higher than that in commercial Penta-BDE mixtures (28%) (Hites et al., 2004), partially due to the debromination of higher brominated congeners. BDE-99 ranged from 31 to 36% in the sediment samples of both Guiyu and Hong Kong was similar to that in commercial product (45%). It seems that the commercial Penta-BDE mixtures used in e-waste was the main contamination source in Guiyu, as the mixtures have been banned in 2004. BDE-153 was an important congener and could serve as a marker in sediment sample along riversides of Nanyang River (NY-I), where rubber printer rollers are burnt discarded. BDE-209 in NY-I was detected at similar levels in NY-II, LJ, and LUT of Hong Kong where total PBDE concentrations in NY-I was up to 1000 times higher than that in other sites. It was revealed that BDE-209 was the most dominant congener in sediments of the PRD, as result of the growth of the electronics manufacturing capacities in the region (Mai et al., 2005).

Mono- to tri-BDEs were detected in sediments from Guiyu and Hong Kong at different concentration levels, with NY-I having the highest (58.5–572 ng/g) among different sites (NY-II and LJ). The figures were alarming and about 500 to 4000 times higher than those (0.13 ng/g) of Tejo River basin of Portugal, which was contaminated by various industries including textile and paper production (Lacorte et al., 2003). In general, di-BDE and tri-BDE were rarely reported in sediment but air samples due to low vapor pressure (Gouin et al., 2002). It is believed that BDE-17 is a breakdown product from possibly from BDE-209 during atmospheric debromination processes (Schecter et al., 2004).

Concentrations of PBDEs measured in fish samples obtained from Guiyu are higher than those reported elsewhere, with tilapia (mixed muscles) from LJ 600 times higher than those from Canadian markets (0.18 ng/g ww) (Tittlemier et al., 2004) and 15000 times higher than from US markets (0.0085 ng/g ww) (Schecter et al., 2004).

PBDE concentrations in bighead carp are even higher than tilapia. Studies on PBDEs in bighead carp are scarce and so comparison could not be made. However, the present results were 10–100 times higher than other studies on different fish species: freshwater fish in markets of Taiwan (30.6 to 281 ng/g lw) (Peng et al., 2006), fresh salmon filet (2.36 ng/g ww) from markets in Belgium (Voorspoels et al., 2006), carp (18 ng/g ww) from the polluted area of Des Plaines River in Belgium (Covaci et al., 2005) and carp (65 ng/g ww) from a river near a manufacturing PUF facility (Dodder et al., 2002), and also higher than those in edible fish (118 and 197 ng/g ww) from rivers located near a BFR manufacturing plant in North East UK (Allchin et al., 1999).

BDE-47 is the predominant congener in fish muscle and liver (de Wit, 2002; Law et al., 2006). A preferential accumulation of PBDE congeners in liver of bighead carp was also observed in pike (Burreau et al., 2000), and marine lean fish (such as plaice, bib and whiting) (Voorspoels et al., 2003).

PBDEs in abdomen, back and tail muscles were detected at different concentrations although similar congener pattern distributions were found (Fig. 3). BDE-47 in tilapia muscles from LJ contributed up to 64.2–68.7% of the total PBDEs, followed by BDE-71 with 10.9%, BDE-28 with 8.1%, BDE-66 with 5.4% and BDE-154 with 5.4%. BDE-28 in fish usually existed in lower proportion in fish according to limited studies (Ikonomou et al., 2002; Zennegg et al., 2003; Law et al., 2003). The congener patterns in tilapia from LUT were slightly different from

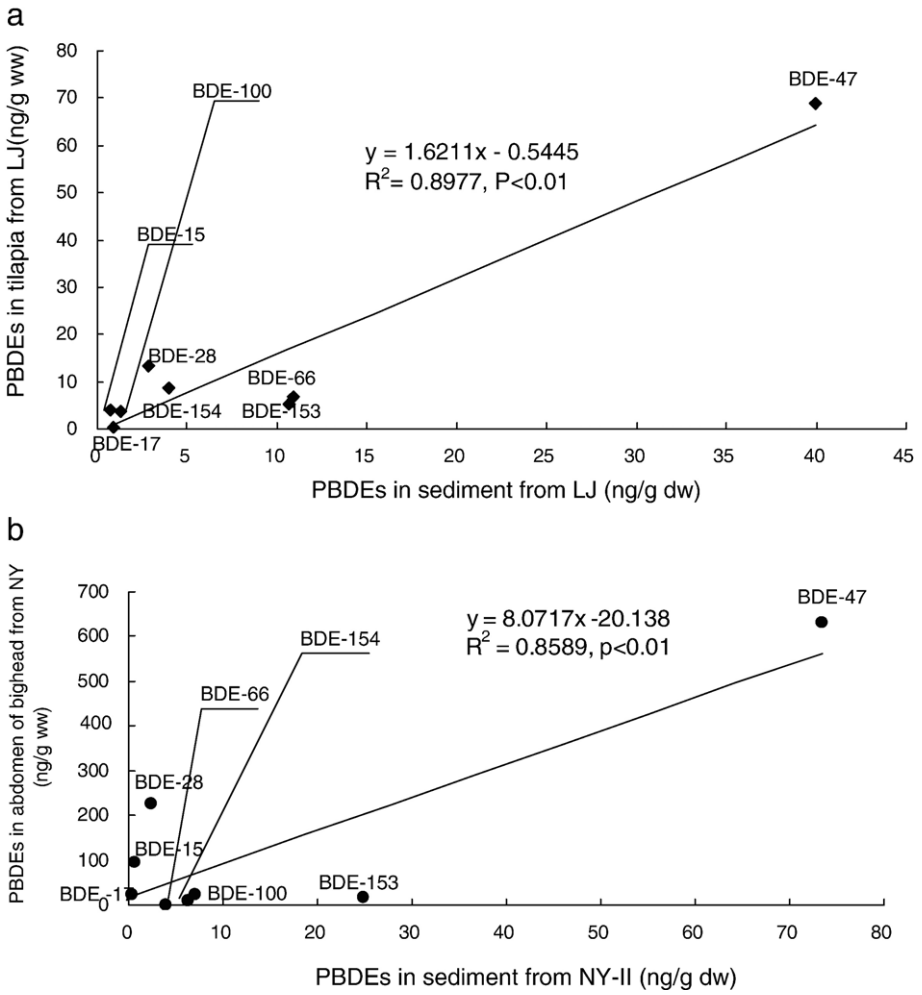

Fig. 4. Correlations between concentrations of PBDEs in fish and sediment: (a) tilapia (mixed muscle) from LJ, and (b) bighead carp (abdomen muscles) from NY-II (bottom sediment).

JL with BDE-47 also the most abundant (57.8% of total PBDEs), followed by BDE-154 with 12.3%, BDE-153 with 5.8% and BDE-100 with 5.8%.

BDE-209 and -183 detected in fish which are commonly found at extremely low levels or even below detection limits (Watanabe and Sakai, 2003; Law et al., 2006). BDE-209 detected in abdomen muscle of tilapia was 0.01 ng/g ww whereas it was not detected in muscle and liver of bighead carp from LJ. It was previously revealed that BDE-209 accumulated in rainbow trout via dietary uptake (Kierkegaard et al., 1999). BDE-183 was only found in tilapia with 0.01 and 0.03 ng/g ww in mixed muscle from LUT and LJ, respectively, and with 0.23 ng/g ww in abdomen muscle but not other fish parts of bighead carp. This indicates that both BDE-209 and -183 tend to accumulate in fish muscle with high lipid content.

PBDE congener patterns were slightly different in tilapia and bighead carp collected from contaminated river. This is due to the fact that the three commercial PBDE products (Penta-, Octa-and Deca-BDEs) would have different uptake and excretion in fish (Hakk and Letcher, 2003). The present results are also in line with the finding that BDE-47 had the greatest uptake by fish (Meerts et al., 2000).

The relationship between concentrations of different congeners with length, wet weight and lipid content of fish samples were investigated. Significant correlation is obtained between total PBDEs concentrations ($r=0.95$ to 0.973, with $p<0.01$) and individual congeners (BDE-28: $r=0.977$ to 0.99, with $p<0.01$; BDE-47: $r=0.929$ to 0.962, with $p<0.01$ to 0.05; BDE-154: $r=0.931$ to 0.958, with $p<0.05$; BDE-153: $r=0.882$ to 0.966, with $p<0.01$ to 0.05) with lipid contents in different parts of

muscle (i.e. abdomen, back and tail). No correlation was observed between total PBDEs concentration in different parts of muscle, except mixed muscle ($r=0.978$, with $p<0.01$) with length of fish.

The PBDE concentrations of tilapias and bighead carps were more than 600 and 200 times higher than those in river bottom sediments collected from the same locations, respectively. This reflected the large fish/sediment concentration ratios for the less brominated congeners (Sellström et al., 1998). Compared with other mechanisms, sediment burial may be a more important sink for heavier congeners, because the heavier congeners have higher sediment–water distribution ratio, which depends heavily on the hydrophobicity of the chemicals as well as the organic matter content of the sediment (Schwarzenbach et al. 2002). On the contrary, lower concentrations of BDE-209 and -183 were found in tilapias and bighead, although higher levels were obtained in sediments, mainly due to their relatively low bioaccumulation potential (Boon et al., 2002).

Fig. 4 shows the correlations between concentrations of individual PBDE congener in fish and sediment. Significant correlations were found between concentrations of low brominated congeners (tri- to hepta-BDEs) (except BDE-99) in fish (different part) and sediment from the same locations, such as that in tilapia and sediment in LJ (Fig. 4a, $r=0.8977$ with $p<0.01$ in mixed muscle), and also bighead carp in NY and sediment in NY-II (Fig. 4b, $r=0.8589$ with $p<0.01$ in abdomen muscle). The major difference between tilapia and bighead carp was possibly due to the large contribution of BDE-28 to total concentrations in bighead carp muscle.

BDE-99 was a special congener detected in fish samples from Guiyu. The level of BDE-99 was higher than in the sediment, because it is the second major constituent of the Penta-BDE commercial products. Similar levels were also obtained in fish from Virginia watersheds (Hale et al., 2001). The low uptake of BDE-99 by carp via oral exposures was lower than the uptake of BDE-47 (Stapleton et al., 2004). Data of fish from Guiyu also reflected different metabolic capacities fish of different species (Wolkers et al., 2004).

5. Conclusion

The present results indicate that the PBDE concentrations in the sediments collected from Guiyu were higher than those from Hong Kong, the Pearl River Delta and other countries. In general, levels of PBDEs in tilapia and bighead carp from Lianjiang River and Nanyang River in Guiyu are 2 or 4 orders of magnitude higher than their counterparts. The highest level of BDE-153 was detected in bank sediments of Nanyang River, which covered with e-waste materials and burnt ash. Different sediment contained e-waste, which consisted of different commercial brominated flame retardants: Penta-BDEs were found at Nanyang River, Octa-BDEs at Lianjiang River and Deca-BDEs at wastewater at Hong Kong. Commercial Penta-BDE mixtures were major brominated flame retardants in e-waste of Nanyang River, commercial Octa-BDE mixtures were in Lianjing River and Deca-BDEs were dominant in wastewater in Hong Kong.

Bioaccumulation of PBDEs is obvious and evident with BDE-47 and -28 at high concentrations in muscles of tilapia and both muscles and liver of bighead carp. BDE-99 had a low uptake in fish from Nanyang River and Lianjiang River. However, it may also due to its rapid depletion in fish after its uptake (Hale et al., 2001; Dodder et al., 2002). Different PBDE congener distributions were found in different sampling locations reflected the predominant commercial PBDE products and their subsequent degradation. Open burning and dumping of e-waste on river bank are the major sources of PBDE contamination in Guiyu, the intense e-waste recycling site since 1995.

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