



Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China

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ABSTRACT

Water and several wild aquatic species including Chinese mysterysnail, prawn, fish, and water snake were collected from a reservoir surrounded by several e-waste recycling workshops in South China. The samples were examined to investigate the levels and bioaccumulation extent of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) released from electronic waste (e-waste) which was processed by crude recycling method. Elevated levels of PBDEs [52.7 to 1702 ng/g wet weight (ww)] and PCBs (20.2–25958 ng/g ww) were found in the collected biota species compared to that in the reference samples (13.0–20.5 ng/g ww for PBDEs and 75.4–82.8 ng/g ww for PCBs). log BAF (bioaccumulation factor) ranged from 2.9 to 5.3 for PBDEs and from 1.2 to 8.4 for PCBs, depending on congeners and species. The relationship between log BAFs and log K_{OW} (octanol–water partition coefficient) can be adequately described by species-specific parabolic models wherein log BAFs generally increased at $\log K_{OW} < 7$ then decreased with further increasing $\log K_{OW}$ both for PBDEs and PCBs. The exceptions were for Chinese mysterysnail and prawn, in which the log BAFs showed a positive linear correlation with $\log K_{OW}$ for PBDEs. Some PBDE and PCB congeners showed BAF values declining from the general trend predicted by K_{OW} , largely attributing to metabolism of these congeners in species sampled.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively over the past two decades as additive brominated flame retardants (BFRs) in most types of polymers applied to computer monitors, television sets, computer cases, wire and cable insulation, and electrical/electronic connectors, at levels ranging between 5 and 30% (de Wit, 2002). Polychlorinated biphenyls (PCBs) were historically used as coolants and lubricants in transformers and capacitors, and as hydraulic and heat exchange fluids in electrical/electronic equipments (EEEs). PBDEs and PCBs contained in EEEs would migrate out when these products were disposed. Excessive release from the obsolete EEEs was one of the important pathways of these chemicals entering the environment (Wong et al., 2007). Once in the environment, most of these substances are persistent in the environment, undergo long-range transport through air or water, and can accumulate in living organisms, thereby, exerting undesirable effects on wild organisms (de Wit, 2002; Watanabe and Sakai, 2003; Hakk and Letcher, 2003). Aquatic organisms are very efficient at accumulating these chemicals through their diet and ambient environment sources, resulting in an

extremely high concentration in their body. The process is called bioaccumulation (Mackay and Fraser, 2000). The degree to which bioaccumulation occurs is normally expressed as bioaccumulation factor (BAF), which is defined as the field-observed ratio of the concentration of a given chemical in biota to the concentration in corresponding water (Streets et al., 2006). PBDEs and PCBs are lipophilic, and octanol is generally considered to be a reasonable surrogate phase for lipids in biological organisms, thus, BAFs should correlate well with octanol–water partition coefficient (K_{OW}) (Fisk et al., 1998; Dimitrov et al., 2002). However, the biological processes in organisms, such as different metabolism rates of these chemicals, would significantly influence this correlation, i.e., BAFs deviated from the general trend predicted by K_{OW} . Chemical-specific, species-specific and site-specific BAFs and their correlations with K_{OW} were always found in field studies, largely due to different metabolism rates of these chemicals which were dependent on both the chemical structure and the metabolic capacity of the organism (Streets et al., 2006; Wang et al., 2007).

Currently, electronic waste (e-waste) is becoming a major environmental concern because of the high generating rate and the potential detrimental impacts on the environment caused by the e-waste-associated toxic chemicals (such as PCBs and PBDEs). In China, most e-waste recycling was processed in informal or illegal

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sectors, even in the backyard workshops, where the recycling operations were conducted using crude methods such as manual disassembly, open incineration and acid dipping (Wong et al., 2007). The local environment had been heavily polluted due to this primitive e-waste recycling activities (Wong et al., 2007). In addition, it was suggested that the PBDEs in sediments (Mai et al., 2005; Wurl et al., 2006) and skipjack tuna (*Katsuwonus pelamis*) (Ueno et al., 2004) from South China Sea might originate from the disposal of e-waste. Although studies have reported the levels of PBDE/PCB in air, dust, soil, sediment and biota samples from the e-waste recycling sites in South China (Wong et al., 2007; Leung et al., 2007; Luo et al., 2007; Liu et al., 2008), no attempt has been made to quantify the levels of these chemicals in water and the extent of their bioaccumulation in aquatic species.

The purpose of this study was to investigate the levels of PBDEs and PCBs in the water and several wild aquatic species from a reservoir surrounded by e-waste recycling workshops in South China, and to assess the extent of bioaccumulation for these pollutants in the wild aquatic species by calculating BAFs from measured concentrations of a large suite of PBDE and PCB congeners in several aquatic species and dissolved water samples. Possible metabolism of these chemicals in the sampled species was also discussed based on the relationship between log BAFs and log K_{OW} .

2. Materials and methods

2.1. Sampling site

The sampling site was located in Longtang Town, Qingyuan City, which was approximately 50 km north of Guangzhou, a major urban center in South China. It was estimated that more than 1300 workshops and 80000 workers had been involved in the business of e-waste dismantling and recycling, and approximately 1.7 million tons of e-waste were dismantled annually in this site. Meanwhile, the traditional agricultures including rice-growing and fish-farming were also practiced around the recycling workshops. Water and wild aquatic species detected in this study were sampled from a reservoir which was surrounded by several e-waste recycling workshops. The remnants including un-wanted parts of the e-waste were dumped along the bank of the reservoir.

2.2. Sample collection

A total of 88 wild aquatic biota samples and three water samples were collected in 2006. Biota specimens consisted of both individual organism and composites of multiple individuals. The wild aquatic species collected in the present study included Chinese mysterysnail (*Cipangopaludina chinensis*; three composite samples from 43 individuals), prawn (*Macrobrachium nipponense*; three composite samples from seven individuals), mud carp (*Cirrhinus molitorella*; seven composite samples from 12 individuals), crucian carp (*Carassius auratus*; six composite samples from 17 individuals), northern snakehead (*Ophicephalus argus*; six individual samples), and water snake (*Enhydrys chinensis*; two individual samples). Reference samples (mud carp, *Cirrhinus molitorella*; five individual samples) were also collected from another reservoir 5 km away from the e-waste recycling workshops, representative of the PBDE and PCB levels in fish with non-point pollution. Biota samples were stored at -20°C until analysis. Water samples were filtered immediately after they were transported to the laboratory.

2.3. Extraction and cleanup

Water sample extraction was according to Streets et al. (2006) with minor modification. In brief, water samples were filtered using ashed glass fiber filters (Whatman, 293-mm GF/F) and the filtered water was passed through a column containing XAD-2 and XAD-4 mix resins (Supelco, Bellefonte, PA, precleaned by successive Soxhlet extraction with methanol and dichloromethane) to retain the organic matter. Each XAD column was spiked with surrogate standards [CBs 65 and 204 for PCBs; CDE 99 (2,2',4,4',5-pentachlorodiphenyl ether), $^{13}\text{C}_{12}$ -PCB 141 and $^{13}\text{C}_{12}$ -BDE 209 for PBDEs], and eluted with 25 mL of methanol followed by 50 mL of dichloromethane. The resins were then transferred into a flask and extracted with methanol (3×50 mL) followed by dichloromethane (3×25 mL) in an ultrasonic bath. Upon addition of 175 mL of saturated NaCl solution, all of the methanol fractions were back-extracted three times each with 50 mL of dichloromethane. The combined dichloromethane fraction was then further extracted with 10 mL of organic free water to remove residual MeOH. The extract was concentrated and solvent exchanged to hexane, and further reduced to approximately 1 mL.

Biota samples were extracted as described in our previous studies (Xiang et al., 2007; Chen et al., 2007). Briefly, after homogenized with ashed anhydrous sodium sulfate and spiked with surrogate standards (mentioned above), the samples were Soxhlet extracted with hexane/acetone (1:1, v/v) for 48 h. The extracts were concentrated, an aliquot of the extract was used to lipid content determination by gravimetric method, another aliquot of the extracts was subjected to gel permeation

chromatography (GPC) to remove lipids. The cleaned extract was concentrated to approximately 1 mL.

The extracts of water and biota samples were further purified by passing through a multilayer silica/alumina column. The extracts were concentrated, solvent exchanged to isooctane, and finally concentrated to 200 μL under a gentle stream of nitrogen. A known amount of internal standard (BDE 118, BDE 128, ^{13}C -PCB 208 for PBDEs and CBs 24, 82, and 189 for PCBs) was added to all extracts prior to instrumental analysis.

2.4. Chemical analyses

2.4.1. GC-MS analysis

PBDEs were analyzed by GC-MS in electron capture negative ionization mode (GC/MS-ECNI) and operated in selected ion monitoring (SIM) mode. A DB-XLB capillary column (30 m×250 μm i.d. ×0.25 μm film thickness) was used to determine the tri- to hepta-BDEs (BDEs 28, 47, 66, 85, 99, 100, 138, 153, 154, and 183). For octa- to deca-BDEs (BDEs 196, 197, 203, 205, 206, 207, 208, and 209), a CP-Sil 13 CB capillary column (12.5 m×250 μm i.d. ×0.20 μm film thickness) was used. The ions m/z monitored for target compounds, surrogate standards, internal standards, and details of the instrument temperature programs were described elsewhere (Mai et al., 2005).

PCBs were quantified by an Agilent 6890 GC coupled with a 5975B Series mass selective detector using an electron impact (EI) ion source. A DB-5 MS column (60 m×250 μm i.d. ×0.25 μm film thickness) was used for separation. The column oven was programmed from an initial temperature of 120 to 180 $^{\circ}\text{C}$ at a rate of 6 $^{\circ}\text{C}/\text{min}$, then ramped to 240 $^{\circ}\text{C}$ at a rate of 1 $^{\circ}\text{C}/\text{min}$, and finally increased at a rate of 6 $^{\circ}\text{C}/\text{min}$ to 290 $^{\circ}\text{C}$ and hold for 15 min. The injector and detector temperatures were maintained at 260 and 230 $^{\circ}\text{C}$, respectively. The electron energy was 70 eV with a scan time of 0.8 s. PCB congeners were monitored at the two most intense ions of the molecular ion cluster. Quantification was based on internal calibration curves made from standard solutions at six concentration levels.

2.4.2. QA/QC

Quality assurance was done by analyses of procedural blanks, blank spikes, and sample duplicates. The recoveries of surrogate standards ($n=45$) were as follows: CDE 99, 78.6%±10.5%; $^{13}\text{C}_{12}$ -PCB 141, 76.3%±6.9%; $^{13}\text{C}_{12}$ -BDE 209, 72.2%±19.8%; PCB 65, 72.6%±6.2%; and PCB 204, 80.2%±6.8%. No surrogate corrections were made to final concentrations. For each batch of 12 samples, a procedural blank and a blank spike (a mixture of 11 PBDE congeners and 23 PCB congeners spiked in blank solvent) were processed. Procedure blanks ($n=5$) contained traces of target chemicals, but the levels were less than 1% of the mass in the samples and they were not subtracted from the sample extracts. The recoveries of the spiking blanks ranged 76.9–105.2% for PBDEs and 65.8–101.5% for PCBs, respectively. Sample duplicates ($n=3$) were analyzed in a similar manner as the biota samples. Relative standard deviations (RSD) of duplicates were less than 15% for all targets except for BDE 209, which was 24%.

The limit of quantification (LOQ) was set as the mean value of targets in procedure blanks plus three times of standard deviations. For the undetectable compounds in blanks, LOQs were estimated based on a signal to noise ratio of 5. LOQs ranged from 0.003 to 0.02 ng/g ww (wet weight) for tri- to hepta-BDEs and from 0.1 to 2.5 ng/g ww for octa- to deca-BDEs, respectively. For PCBs, the LOQs ranged from 0.02 to 0.32 ng/g ww.

3. Results and discussion

3.1. Levels and congeners distribution of PBDEs and PCBs

Selected PBDE and PCB congener concentrations, ΣPBDEs (the total concentrations of the 18 PBDE congeners measured) and ΣPCBs (sum concentrations of the 44 PCB congeners detected) in water, aquatic species and reference samples were summarized in Table 1.

3.1.1. Water

The dissolved phase water concentrations of individual PBDE congeners ranged from non-detected to 10.9 ng/L, which were similar with those for individual PCB congeners measured (non-detected to 42.3 ng/L). However, ΣPBDEs (24.4 ng/L) was almost one order of magnitude lower than ΣPCBs (204 ng/L) in the water samples (Table 1). ΣPBDEs in our study was approximately 50 times higher than the highest level in water samples reported previously (0.51 ng/L) (Oros et al., 2005), despite the latter included both dissolved and particulate phases. ΣPCBs in the present study exceeded the established USEPA water quality standard (using Aroclor analysis) for human health protection of 0.17 ng/L (USEPA, 1999) by more than 1000 folds. BDEs 47, 28, 99, 66, and 100, and CBs 28/31, 18, 17, 8/5, 52, 44, and 19 were the dominant congeners, which collectively accounted for more than 90% and 70% of ΣPBDEs and ΣPCBs , respectively. This result was consistent with the relative high water solubility for lower chlorinated/brominated congeners and was accordant with other studies (Howell et al., 2008; Streets et al., 2006).

3.1.2. Wild aquatic species

Large inter-specific variations were found in PBDE and PCB concentrations (Table 1). The highest ΣPBDEs value was found in water snake (1091 ng/g ww), followed by mud carp (830 ng/g ww), northern snakehead (490 ng/g ww), crucian carp (316 ng/g ww), prawn (254 ng/g ww) and Chinese mysterysnail (67.5 ng/g ww). Like in the water, ΣPCBs were one order of magnitude greater than ΣPBDEs in aquatic species. ΣPCBs were greatest in water snake followed by mud carp, crucian carp, northern snakehead, prawn, and Chinese mysterysnail containing 16512, 12390, 8338, 7052, 3503 and 62.8 ng/g ww, respectively. The variations of PBDE/PCB concentrations in different species may

Table 1

Concentrations (median and range) of selected congeners of PBDE and PCB, Σ PBDEs, and Σ PCBs in water (ng/L), aquatic species and reference samples (ng/g ww) collected from a reservoir in an e-waste recycling site in South China^a

	Water	Water snake	Northern snakehead	Mud carp	Crucian carp	Prawn	Chinese mysterysnail	Reference mud carp
BDE 28	5.03 (4.92–5.14) ^b	6.29 (2.08–10.5)	40.1 (26.2–60.1)	74.7 (54.9–170)	21.1 (2.11–35.7)	15.4 (6.01–17.9)	4.38 (3.47–7.69)	2.81 (2.73–3.73)
BDE 47	10.7 (10.5–10.9)	507 (266–748)	310 (270–394)	400 (187–1283)	215 (22.8–335)	120 (61.6–127)	20.0 (16.7–38.1)	9.53 (8.21–13.1)
BDE 99	3.22 (3.18–3.26)	121 (29.7–213)	0.26 (nd ^c –4.58)	5.52 (0.98–53.5)	1.30 (0.48–22.1)	14.4 (12.6–34.8)	16.9 (10.8–37.0)	0.02 (0.01–0.94)
BDE 100	1.0 (0.98–1.01)	130 (72.2–188)	78.0 (43.0–120)	47.3 (20.7–168)	22.9 (5.31–86.4)	26.5 (11.6–37.1)	4.72 (4.42–6.54)	0.39 (0.34–0.49)
BDE 153	0.44 (0.43–0.44)	143 (53.9–232)	3.22 (nd–16.7)	66.0 (18.0–97.8)	8.03 (3.87–36.4)	12.2 (10.1–18.7)	6.06 (3.65–6.20)	0.13 (0.11–0.66)
BDE 154	0.79 (0.76–0.82)	90.0 (42.6–137)	55.9 (32.6–76.9)	64.2 (21.2–95.5)	18.7 (7.84–66.9)	16.7 (6.94–21.6)	4.89 (3.89–6.28)	0.32 (0.01–0.41)
BDE 138	0.60 (0.48–0.72)	7.58 (0.61–14.6)	6.00 (nd–21.9)	6.36 (nd–27.3)	17.5 (0.29–59.2)	10.5 (9.36–14.6)	nd	0.18 (0.14–0.35)
BDE 209	0.41 (0.40–0.41)	13.0 (2.38–23.6)	0.86 (0.65–1.30)	138 (0.80–549)	4.73 (2.31–136)	15.0 (2.81–47.7)	nd	0.45 (nd–6.53)
Σ PBDEs ^d	24.4 (23.8–25.0)	1091 (480–1072)	490 (372–714)	830 (305–830)	316 (46.6–853)	253 (131–363)	67.5 (48.4–115)	14.0 (11.7–27.1)
PCB 28/31	41.8 (39.9–42.3)	178 (78.6–277)	151 (50.9–755)	1000 (318–1324)	403 (81.6–1210)	399 (307–408)	1.50 (0.42–21.6)	3.76 (2.43–5.02)
PCB 52	11.3 (10.8–11.3)	601 (158–1044)	203 (122–1149)	675 (250–1194)	599 (107–1408)	66.9 (41.8–90.9)	1.77 (0.37–16.6)	2.05 (1.42–2.49)
PCB 101	2.99 (2.77–3.02)	1132 (551–1713)	609 (402–1328)	1009 (528–1869)	631 (138–1323)	107 (62.3–159)	3.39 (1.08–17.7)	1.97 (1.41–2.35)
PCB 118	1.76 (1.63–1.87)	859 (556–1162)	861 (461–1264)	912 (500–1590)	560 (107–1129)	429 (233–598)	2.83 (0.94–15.6)	2.67 (2.25–3.13)
PCB 138	0.89 (0.71–0.93)	1678 (802–2555)	751 (512–1015)	720 (432–1066)	451 (108–983)	283 (168–420)	2.64 (0.89–12.5)	2.20 (1.72–2.54)
PCB 153/132	1.14 (0.99–1.17)	1768 (872–2663)	763 (560–1109)	955 (589–1172)	549 (152–1105)	238 (149–409)	3.71 (1.13–13.5)	2.49 (1.72–2.77)
PCB 180/193	0.09 (0.09–0.11)	513 (176–851)	137 (89.6–184)	121 (98.8–159)	71.7 (30.8–150)	45.0 (40.0–103)	0.59 (0.21–1.90)	0.69 (0.53–0.76)
Σ PCBs ^e	204 (196–206)	16512 (7067–25958)	7052 (4664–16244)	12390 (6983–19588)	8338 (1963–18174)	3503 (2204–4734)	62.8 (20.2–293)	75.7 (67.8–82.8)

^a The selected PBDE congeners in the table are those each accounting more than 1% of total PBDEs in biota, selected PCB congeners are seven indicator PCBs.

^b Concentration ranges.

^c Non-detected.

^d Sum of 18 PBDE congeners measured (BDEs 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 205, 206, 207, 208, and 209).

^e Sum of 44 PCB congeners detected (CBs 8/5, 17, 18, 19, 22, 26, 28/31, 37, 41, 42, 44, 47/48/75/38, 52, 60, 66/95, 70, 71, 74, 87/115, 99, 101, 105, 110, 118, 128, 131, 138, 146/61, 147, 153/132, 157, 164/163, 170/190, 171, 172, 177, 180/193, 183, 187, 199, 203/196, 207, 208, and 209).

attribute to the different trophic position and specific feeding ecology of these species. Generally, water snake and northern snakehead are voracious predatory species and have higher trophic positions than other species sampled, resulting in elevated PBDE and PCB levels in their bodies. Mud carp feed on organic detritus or decomposed organic matter and like to stir up bottom sediments during feeding. Typically increasing organic pollutant concentrations in decomposed organic matter (deBruyn and Gobas, 2004) and surficial sediment render them prone to higher PBDEs and PCBs exposure.

Total PBDE and PCB concentrations in mud carp were 164 times and 59 times higher than that in the reference mud carp samples (Table 1), suggesting that aquatic species were subjected to heavy pollution of PCBs and PBDEs, because of the crude e-waste recycling activities. Σ PBDEs in fish were higher or comparable to that in fish from Guiyu (35.1–1088 ng/g ww) (Luo et al., 2007), another notorious e-waste recycling site in South China (Wong et al., 2007). Median values of Σ PCBs in all aquatic species were 3–825 times greater than the USEPA screening value of 20 ng/g ww (USEPA, 2000) and were at the high end of the worldwide range (Domingo and Bocio, 2007). It should be pointed out that the reference samples had also been contaminated by PCBs and PBDEs, with levels markedly higher than concentrations in edible fish from South China (non-detected to 7.65 ng/g ww for PCBs and non-detected to 3.85 ng/g ww for PBDEs) (Meng et al., 2007). There was no point source around the reservoir the reference fish sampled, the relatively high concentrations of PBDEs and PCBs in reference fish were possibly due to the air transportation.

A significant correlation was found between Σ PBDEs and Σ PCBs in aquatic species ($R=0.63$, $P<0.0005$, $n=27$, Fig. 1), indicating that these two types of chemicals were being acquired from the same source (e-waste) and that the net uptake rates of PBDEs and PCBs by the aquatic species in this study were comparable.

BDEs 28, 47, 100, 153 and 154 were the dominant congeners in all species, collectively accounting for 61% to 98% of the total PBDEs. This was also observed from other studies on freshwater fishes (de Wit, 2002). BDE 28 contributed to 5.9–12% in aquatic species except for water snake, in which BDE 28 accounted for 0.5%, likely due to the low assimilation efficiency of BDE 28 in this species. BDE 99 accounted for 9.3–26.7% of Σ PBDEs in water snake, prawn, and Chinese mysterysnail; while it constituted only 0.05–0.6% in fish. The metabolism of BDE 99 in these fish may be responsible for the observation (Stapleton et al., 2004b; Stapleton et al., 2004c).

The dominant PCB congeners in aquatic species included CBs 153/132, 118, 138, 101, 110, 28/31, 52, 99, and 105, collectively representing 42–59% of Σ PCBs. This result supports the observation that certain penta- and hexa-PCBs contribute a large proportion of the total PCB concentrations in aquatic species (Metcalf and Metcalf, 1997). However, water snake and northern snakehead had lower fractions of CBs 28/31 and 52 and greater fractions of CBs 153/132 and 138 compared to other species, possibly due to the preferential bioaccumulation of more chlorinated congeners in upper trophic level organisms (Kay et al., 2005). CB 209 was found in 47% of the biota samples with level ranging from 0.2 to 15.5 ng/g ww in the present study. This congener was only sporadically detected in the environment and biota samples (Kannan et al., 1997; Howell et al., 2008). The comparatively high detectable frequency of CB 209 in our samples indicated that a special source, like technical Aroclor 1268 (Kannan et al., 1997), was present in this e-waste site.

3.2. Bioaccumulation in wild aquatic species

3.2.1. BAFs in aquatic species

To better understand the extent of bioaccumulation of PBDEs and PCBs, BAFs were calculated for individual congeners in aquatic species. The calculated BAFs varied among species and chemicals. Log BAFs ranged from 2.9 to 5.3 for PBDEs and 1.2 to 8.4 for PCBs, with the lowest value for BDE 28 and CB 17 in Chinese mysterysnail, and the highest value for BDE 154 and CB 153/132 in water snake. The log BAF values in the present study were agreed with those reported in aquatic species from a lake receiving effluent from sewage treatment plant in China, which have log BAF values of 2.2 to 6.5 for PBDEs and 2.5 to 5.5 for PCBs (Wang et al., 2007). Streets et al. (2006) reported log BAF ranges of 6.7–7.5 for PBDEs and 5.5–8.5 for PCBs in lake trout from Lake Michigan (Streets et al., 2006), which were considerably greater than our values. Differences in metabolism capacities between species and environmental conditions studied [e.g., higher water temperature and PCB levels in our study, which both could enhance the metabolism rates of PCBs in fish (Buckman et al., 2007)] could likely cause such a discrepancy. BAFs for PBDEs were slightly lower than that for PCBs, reflecting reduced bioavailability or other kinetic limitations to uptake, or enhanced depuration including biodegradation and non-metabolic routes (e.g., fecal excretion) for PBDEs in these

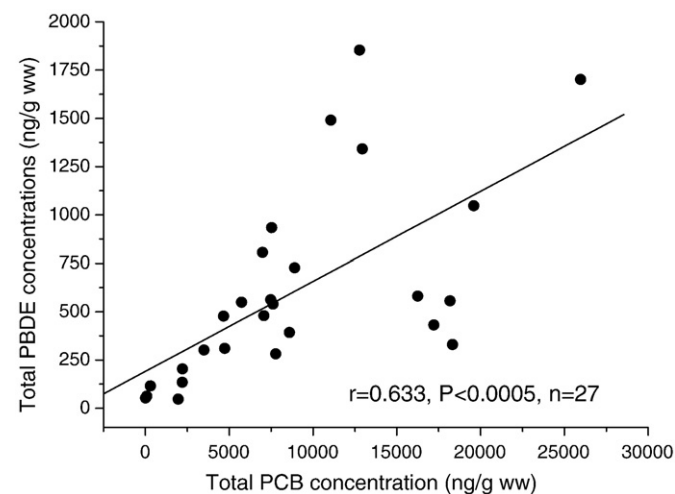


Fig. 1. Relationship between total PBDE and PCB concentrations in wild aquatic species from a reservoir in an e-waste recycling site in South China.

species and/or their underlying food web. This finding was consistent with the report of Streets et al. (2006) who observed that the BAF values for PBDEs were lower than those for PCBs with similar K_{OW} in lake trout (Streets et al., 2006). However, PBDEs were generally found to have a higher bioaccumulation potential compared to PCBs with similar K_{OW} in other studies (Wang et al., 2007; Stapleton et al., 2004c).

3.2.2. Relationship between log BAFs and log K_{OW}

The log BAF was plotted versus log K_{OW} for PBDEs and PCBs in the aquatic species in Fig. 2. The BAFs for PCBs increased with increasing K_{OW} at log $K_{OW} < 7$, and subsequently declined with a further increase of log K_{OW} in all species sampled. This trend was also observed and explained in other studies (Wang et al., 2007; Kannan et al., 1998). For PBDEs, the trend was similar with that for PCBs in all species except for Chinese mysterysnail and prawn, in which BAFs showed a linear increase with increasing K_{OW} (Fig. 2 e and f). It may attribute to the less efficiency of debromination and elimination of PBDEs in the two species. The trends for PBDEs were different from Wang et al. (2007) who observed that BAF values decreased with increasing K_{OW} values in aquatic species (Wang et al., 2007).

A highly significant relationship ($P < 0.0005$) was found from the plot of log BAFs versus log K_{OW} for PCBs in all species (Fig. 2), with higher correlation coefficients in

predator (water snake and northern snakehead, Fig. 2 a and d). For PBDEs, very strong correlations ($R^2 = 0.622–0.998$) between log BAFs and log K_{OW} were observed when some possible metabolic congeners (BDEs 85 and 99) were excluded, although the correlations were not significant in mud carp and prawn (Fig. 2 b and f).

There were many data points that diverged from the general trend predicted by K_{OW} . CBs 26, 70, 101, 110, and 136 had markedly lower BAFs than other congeners with similar K_{OW} in all species. These congeners were found to be metabolized to methylsulfonyl PCBs in deepwater sculpin (Stapleton et al., 2001), although this metabolism capacity was lower in invertebrates and fish. CB 37, a non-ortho-substituted congener, also had a significantly smaller BAF than CBs 42, 44, and 52, having similar log K_{OW} values (about 5.8), possibly attributing to metabolism. A probable induction of detoxification mechanism for non-ortho-substituted PCBs was found in sea stars (Danis et al., 2006). In contrast, CBs 153, 138, 118, 180, 128, 105, and 170, congeners with recalcitrant structure resisting to metabolism, had greater BAFs than other congeners with similar K_{OW} .

BDEs 99 and 85 were depressed from the general trend in all species except for Chinese mysterysnail (Fig. 2). BDE 99 had been proved to be metabolized in fish (Stapleton et al., 2004b; Stapleton et al., 2004c). The ratios of BDE 47/BDE 99 in our fish samples (82, 94, 1431 for mud carp, crucian carp, and northern snakehead, respectively)

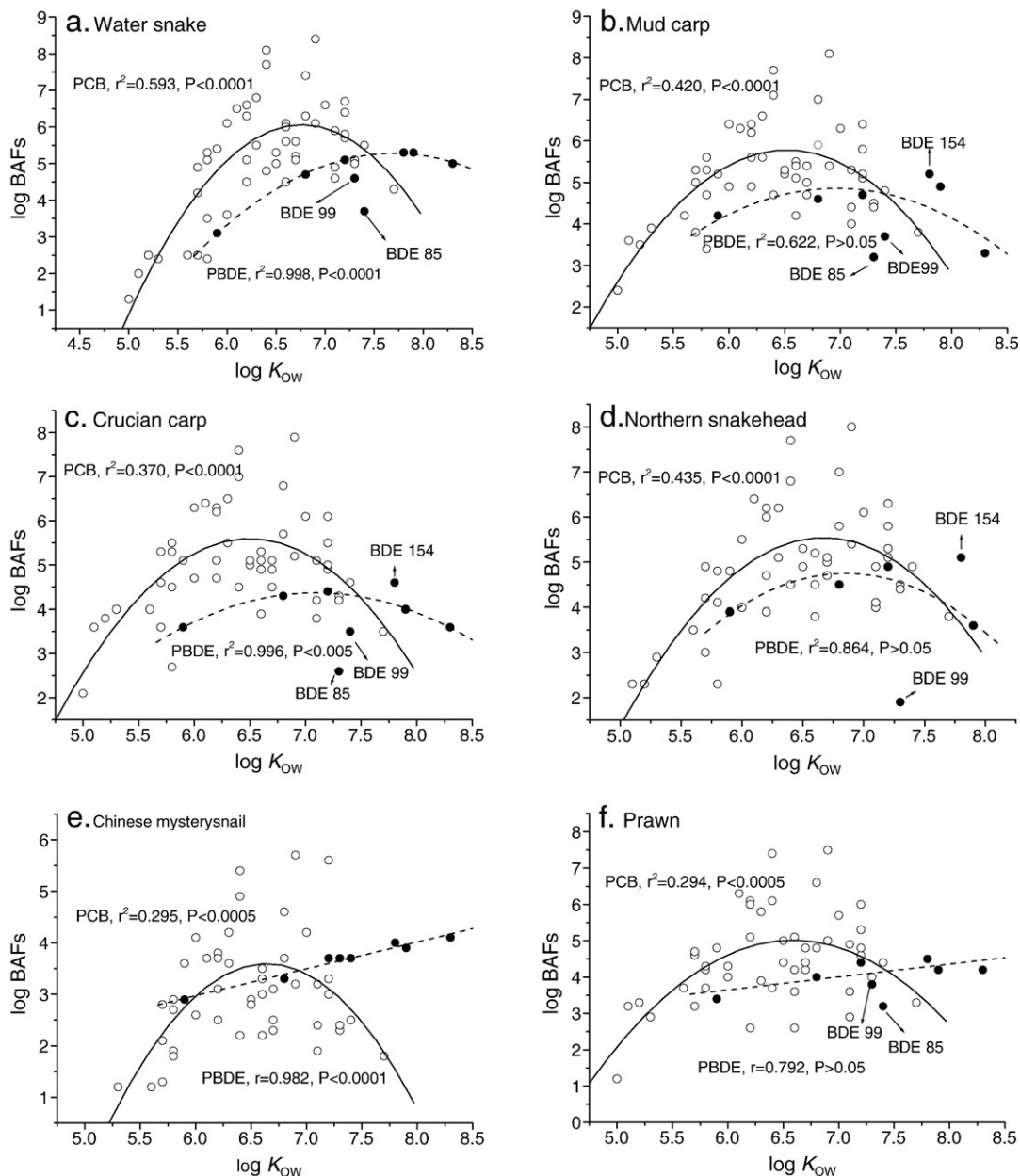


Fig. 2. Log BAF versus log K_{OW} for PBDE (filled circles) and PCB (open circles) congeners in wild aquatic species. Solid and dashed lines are the fit curves for all PCB congeners detected and possible non-metabolic PBDE congeners (BDEs 28, 47, 100, 153, and 183), respectively. Log K_{OW} values are taken from Hawker and Connell (1988) for PBDEs and from Braakevelt et al. (2003) for PCBs.

were much higher than that in water (3.3), suspended particulate mater (0.93, unpublished data), sediments (0.96, unpublished data), and other species detected (1.2–5.3), whereas BDE 47/BDE 100 ratios were remarkably constant among the environment medias and various species (4–10), indicating possible metabolism of BDE 99 in these fish. There was little information on the metabolism of BDE 85 in organisms. Tomy et al. (2004) assumed that BDE 85 was metabolized in lake trout by comparing its half-lives to chemicals with a similar K_{OW} (Tomy et al., 2004). Wolkers et al. (2004) found that BDE 85 was diminished in ringed seals from arctic area in contrast to their food (Wolkers et al., 2004). The decline of log BAF for BDE 85 in water snake, fish, and prawn might be also due to its metabolism in these species. Contrasting to the decline of BAFs for BDEs 99 and 85, the BAF values for BDE 154 were bullish from the general trend in fish (Fig. 2 b, c and d). Similarly, the relative abundance of BDE 154 in fish (7.6–10.5%) was higher than those in water and sediment (1.8–4.3%). BDE 154 was reported to be a metabolic product of BDE 209 in fish (Tomy et al., 2004; Stapleton et al., 2004a), our results also suggested that the biotransformation of BDE209 might contribute, in part, to the enhanced BAF value of BDE 154 in fish.

4. Conclusions

Elevated levels of PBDEs and PCBs in water and aquatic species samples suggested the environment and biota in the study area had been heavily polluted by these chemicals because of the un-regulated e-waste recycling activities. Lower BAFs for PBDEs and PCBs were found in aquatic species compared to other studies, likely due to the difference in metabolism capacity between species and the different environmental conditions studied. Some congeners diverged from the general trend predicted by log K_{OW} , largely attributing to the difference in metabolism rates of these congeners in species sampled.

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