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Polybrominated diphenyl ethers (PBDEs) in free-range domestic fowl from an e-waste recycling site in South China: Levels, profile and human dietary exposure

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ABSTRACT

To evaluate the status of polybrominated diphenyl ethers (PBDEs) contamination in poultry and sequentially human exposure through consumption of poultry in an e-waste recycling site in South China, two kinds of free-range domestic birds, chicken and duck, were collected and their muscle and liver tissues were analyzed for 16 PBDE congeners. Chicken shows higher PBDE concentrations (summation of 16 PBDE congeners) in both muscle and liver tissues, ranged from 5.7 to 4381 and from 1.5 to 7897 ng/g (lipid weight, the same hereinafter), respectively, compared to duck, ranged from 2.4 to 51 and from 1.9 to 134 ng/g. Different living habitat and feeding habits between the two species might be responsible for this observation. No sex-related differences in PBDE concentrations were found for the two species, while the PBDE concentrations in muscle were higher than those in liver for chicken. The PBDE concentrations in muscle of chicken in the present study were higher than the levels of PBDEs in chicken from other studies reported by far. BDE209 and nona-BDEs were the major congeners in poultry. Comparison of PBDE profiles between birds and environmental matrix implied that the biodebromination of BDE209 might occur in poultry. The intake of PBDEs through consumption of poultry ranges from 7.8 ng/day to 3582 ng/day with a medial 68 ng/day, which is comparable to the calculated values through consumption of all foodstuffs in other studies. The present study suggested that the total dietary PBDEs intake for local residents might be considerably enhanced due to the e-waste recycling activity.

1. Introduction

Electronic waste (e-waste), a term referring to discarded electrical and electronic equipment, is becoming a major environmental concern recently, particularly in developing countries (Leung et al., 2007; UNEP, 2005). As noted by UNEP (2005), there were 20–50 million tones of e-waste generated per year around world. It has been estimated that 50–80% of the global e-wastes is legally or illegally imported to Asia, 90% of which destining for China (Puckett et al., 2002). The unregulated e-waste recycling activities in these regions have led to the release of various hazardous chemicals into surrounding environment, of which, PBDE is one of the most concerns because the e-wastes contain significant levels of flame retardants made of various PBDE products. PBDEs are highly hydrophobic, persistent in the environment, and can bioaccumulative in biota and humans. Although there are virtually no data on the effects of PBDEs on human health, animal studies indicate that PBDEs, including tetra-, penta-, hexa-, and deca-BDEs, have endocrine disruption, reproductive/developmental effects and neurotoxicities (Eriksson et al., 2002; Meerts et al., 2000; Stoker et al., 2005; Viberg et al., 2003; Zhou et al., 2002). Currently, several studies measured PBDEs in various environment media (such as soil, atmosphere, and sediment) and human serum samples collected from Guiyu, one of the largest e-waste recycling sites in Guangdong Province, China. Very high concentrations of PBDEs were found in combusted residue samples (33,000–97 400 ng/g, dry wt) and human serum samples (140–8500 ng/g, lipid wt) (Bi et al., 2007; Leung et al., 2007; Wang et al., 2005). Recently, we have determined the PBDE levels in biological environmental samples collected from Qingyuan, the second largest e-waste site in Guangdong Province (Liu et al., submitted for publication). However, the limited species sampled and sample numbers in that survey (only eighteen samples for five species) were insufficient to evaluate the contaminant status, distribution patterns, and effects.

Birds have been applied as sentinel species for monitoring levels and effects of persistent organic pollutants (POPs) in both aquatic and terrestrial ecosystems (Chen et al., 2007; Naert et al., 2007; Voorspoels et al., 2006a). Indeed a rapid increase of PBDE concentrations was observed in birds' eggs from the Great Lakes from 1981 to 2000 (Nortstrom et al., 2002) and the Baltic Proper from 1970 to 1989

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(Sellström et al., 1993). These increasing trends were coincident with those observed for people and other mammals (Hites, 2004). In general, wild birds are used to monitor the POPs contamination on relative large geographic scales. Domestic bird tends to reside in a small-scale area. The contaminants measured from domestic birds may provide an indication of relatively fine-scale differences in localized pollutions.

Taking the above into account, the purpose of the present study was to extend the data obtained in our previous survey (Liu et al., submitted for publication). The levels of PBDEs were measured in 51 free-range domestic birds (chicken and duck), which were raised within the Qingyuan e-waste recycling site, to monitor the PBDEs pollution status. The distributions of PBDE concentrations and congener profiles between sexes and between tissues in these species were investigated. From a human health point of view, chicken and duck were the common constituents of the diet of humans. Thus, there is considerable potential for exposure to PBDEs via the diet for people living in the e-waste recycling sites. The daily intake of PBDEs by local population through consumption of poultry is also estimated in present study.

2. Materials and methods

2.1. Study area

The e-waste site is located in Qingyuan County, Guangdong Province, 50 km north away of Guangzhou, a major urban center city in South China. This site hoses more than 1300 dismantling and recycling workshops within two of the administrative towns, Longtang and Shijiao, and covers an area of about 3.3 km^2. It was estimated that more than 80,000 workers were engaged in the recycling activities and approximately 1.7 million tons of e-wastes, which included computers, printers, cables, TV-sets, electromotor, electrical machines, transformers et al., were dismantled annually in this site (http://www.21class.com/ccer/html/14050-1.shtml). Traditional agriculture, such as rice growing, vegetables planting, fish farming, and poultry rising, is still practiced in farmlands surrounding the dismantling workshops.

2.2. Sampling and analysis

Free-range chickens (*Gallus domesticus*), 16 cocks and 17 hens, and free-rang ducks (*Anas platyrhynchos domesticus*), 9 females and 9 males, were purchased from farmers living in Longtong and Shijiao towns. Free-range domestic chickens and ducks were raised in the field around the farmer's house and fish ponds, respectively, with nine to ten months of age. Considering local farmland grain was the major food item of the domestic birds, about 250 g of grain which was used to feed the poultry was purchased from each farmers, and they were mixed together to get three composite samples for analyze. Three composite surface soil samples were also collected from ground around the farmer's house where the chickens roamed using a straw brush from the surface of the soils.

After being transported to the laboratory, chickens and ducks were euthanized and liver, pectoral muscles were excised. Tissue, grain and soil samples were stored at −20 °C until sample preparation. After freeze-dried, about 0.2–5 g of homogenized tissue sample, 10 g of ground grains and 15 g of meshed soil were transferred into an extraction thimble, respectively. PCB 209 and ^{13}C-PCB 141, obtained from Ultra Scientific (North Kingstown, RI) and Cambridge Isotope Laboratories (Andover, MA), respectively, were spiked as surrogate standards. Lipids and PBDEs were isolated from the raw material by Soxhlet extraction with 200 mL hexane/acetone (1:1, v/v) for 48 h. The lipid content was determined by gravimetric measurement from an aliquot of extract. Another aliquot of extract used for PBDEs analysis was subject to gel permeation chromatography, with a 50 cm×2.5 cm i.d. glass column (with a PTFE stopcock) packed with 40 g SX-3 "Bio-Beads" (Bio-Rad Laboratories, Hercules, CA), and eluted with dichloromethane/hexane (1/1 in volume) for lipid removal. Eluate from 120 to 280 mL containing PBDEs was collected and concentrated to 1 mL with a rotary evaporator. The concentrated extract was further cleaned and fractionated on a 10-mm i.d. silica/alumina column packed from bottom to top with neutral alumina (6 cm, 3% deactivated), neutral silica gel (2 cm, 3% deactivated), 25% sodium hydroxide silica (5 cm), neutral silica gel (2 cm, 3% deactivated), 50% sulfuric acid silica (8 cm), and anhydrous sodium sulfate (1 cm). The PBDEs were eluted with 70 mL of 50% dichloromethane in hexane, and the extract was concentrated with a rotary evaporator to a small volume, further concentrated to near dryness under a gentle nitrogen flow, and redissolved in 50 µL of isooctane. A known amount of internal standard (^{13}C-PCB 208, purchased from Cambridge Isotope Laboratories) was added to all extracts prior to instrumental analysis.

PBDEs were analyzed by gas chromatography-electron capture negative ionization-mass spectrometry (GC-ECNI-MS) operated in the selected ion monitoring (SIM) mode. Details of the instrumental conditions are published elsewhere (Mai et al., 2005). For tri- to hepta-BDE congeners (BDE28, 47, 66, 100, 99, 85, 154, 153, and 183), a 30 m×0.25 mm×0.25 µm DB-XLB capillary column was used and ions m/z=79, 81 were monitored. For the analysis of octa- to deca-BDEs (BDE197, 203,196, 208, 207, 206, and 209), a 12.5 m×0.25 mm×0.20 µm CP-Sil 13 CB capillary column was used, Ions m/z=79, 81 were monitored except for BDE209, for which m/z=486.7, 488.7 were used. For surrogate standards ^{13}C-PCB141 and PCB209, ions m/z=372/374/376 and 496/498/500 were monitored, respectively. In addition, m/z=474/476/478 were monitored for the internal standard, ^{13}C-PCB 208.

2.3. Quality control

Quality assurance and quality control procedures included regular injection of solvent-prepared standard solutions, procedural blanks, spiked blanks (11 PBDEs: BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, and 209 spiked into solvent) and duplicate extractions for each bath of 12 field samples to monitor for quantitative reproducibility and instrument sensitivity. An aliquot of BDE 209 standard at 2 ng was also injected daily to check possible degradation of BDE 209 during the short column analysis, and the degradation ratio must be less than 5% before sample was injected. Procedural blanks contained traces of BDE47 (an average of 0.6 ng) and BDE209 (an average of 0.8 ng), which were less than 10% of the mass in the samples and were appropriately subtracted from sample extracts. Mean (±standard error) recoveries of 11 PBDE congeners in three spiked blank samples were as follows: BDE28 (70±7%); BDE47 (78±9%); BDE66 (84±9%); BDE100 (71±7%); BDE99 (84±9%); BDE85 (96±10%); BDE154 (78±8%); BDE153 (91±11%); BDE138 (97±12%); BDE183 (91±13%); BDE209 (95±5%). The recoveries of surrogate standards, added to the sample prior to extraction were in the range of 65%–114% (mean 92%) for ^{13}C-PCB141, and 75%–122% (mean 98%) for PCB209. The duplicate extractions and injections demonstrated on average 15% and 5%, respectively, analytical

Table 1
Median concentration and range of PBDEs in bird samples (in ng/g lipid) and grain and soil samples (in ng/g dry weight)

	Cock (n=16)		Hen (n=17)		Male duck (n=9)		Female duck (n=9)		Grain (n=3)	Soil (n=3)
Compound	Muscle	Liver	Muscle	Liver	Muscle	Liver	Muscle	Liver	Mean±STD	Mean±STD
Lipid(%)	9.8(6.5–12.5)	28.9(22.5–58.7)	7.6(6.1–16.8)	24.7(16.4–54.5)	14.1(9.1–17.4)	27.8(22.9–45.9)	15.1(9.8–18.8)	30.3(28.7–40.3)		
BDE28	0.1(nd–2.5)	<0.1(nd–0.1)	<0.1(<0.1–0.4)	<0.1(nd–0.3)	<0.1(<0.1–0.1)	<0.1(nd–0.2)	<0.1(<0.1–0.1)	<0.1(<0.1–0.4)	0.03±0.001	0.5±0.17
BDE47	2.6(0.1–87)	0.8(0.1–3.4)	1.1(0.2–9.2)	0.4(<0.1–10)	0.3(0.1–1.6)	0.3(0.2–3.8)	0.1(<0.1–1.3)	0.3(<0.1–3.4)	0.16±0.01	8.5±0.35
BDE66	0.2(nd–2.3)	<0.1(nd–1.0)	<0.1(<0.1–0.5)	<0.1(nd–4.0)	<0.1(<0.1–0.3)	<0.1(nd–0.3)	<0.1(nd–<0.1)	<0.1(<0.1–0.9)	0.04±0.001	0.9±0.29
BDE100	0.8(0.1–11)	0.2(nd–3.0)	0.3(<0.1–1.9)	0.2(<0.1–4.7)	0.1(<0.1–0.4)	0.1(<0.1–0.7)	<0.1(<0.1–0.2)	<0.1(<0.1–0.7)	0.04±0.007	2.5±0.75
BDE99	3.5(0.1–30)	0.5((0.1–6.2)	0.9(0.2–15)	0.4(<0.1–14)	0.4(<0<.1–1.9)	0.4(<0.1–3.1)	0.2(<0.1–0.8)	0.3(<0.1–4.4)	0.11±0.001	15.7±4.0
BDE85	0.3(nd–0.9)	<0.1(nd–0.2)	0.1(nd–1.3)	<0.1(nd–0.4)	<0.1(<0.1–0.4)	<0.1(<0.1–0.4)	<0.1(nd–0.3)	<0.1(nd–0.2)	0.01±0.001	0.8±0.1
BDE154	0.4(nd–7.2)	0.3(nd–45)	0.2(<0.1–1.3)	0.1(nd–3.2)	<0.1(<0.1–0.3)	0.1(<0.1–0.5)	<0.1(nd–0.2)	<0.1(<0.1–0.7)	0.03±0.001	1.5±0.13
BDE153	0.8(nd–40)	0.4(<0.1–380)	0.6(0.1–2.1)	0.2(nd–4.4)	0.1(<0.1–0.5)	0.2(<0.1–1.0)	<0.1(<0.1–0.2)	0.1(<0.1–2.2)	0.02±0.001	3.2±0.66
BDE183	1.4(0.1–254)	0.9(0.2–3570)	1.3(0.1–5.2)	0.5(<0.1–3.8)	0.3(nd–1.1)	0.3(0.1–2.8)	0.1(<0.1–0.4)	0.2(0.1–7.0)	0.03±0.001	4.3±1.7
BDE197	nd(nd–1.1)	nd(nd–4.9)	nd(nd–1.0)	nd(nd–0.1)	nd(nd–0.4)	0.1(nd–0.5)	n<d(nd–0.2)	0.1(<0.1–2.7)	0.09±0.003	3.8±0.47
BDE203	0.7(0.1–105)	0.7(<0.1–162)	0.7(<0.1–3.3)	0.5(<0.1–4.3)	0.1(<0.1–0.8)	0.2(nd–0.4)	<0.1(<0.1–0.5)	0.2(<0.1–1.3)	0.19±0.01	4.1±0.90
BDE196	1.1(0.1–203)	1.3(0.2–408)	1.0(0.2–3.6)	0.4(<0.1–4.7)	0.1(<0.1–0.9)	0.3(nd–0.5)	<0.1(<0.1–0.6)	0.2(<0.1–1.7)	0.14±0.01	3.4±0.35
BDE208	3.1(0.6–475)	2.9(0.3–286)	2.5(0.5–11)	1.5(0.2–25)	0.4(0.2–2.1)	0.6(nd–2.3)	0.3(0.1–2.4)	0.4(0.1–2.4)	0.73±0.01	7.4±2.2
BDE207	7.9(1.2–1476)	6.9(0.9–2187)	7.3(0.8–24)	4.5(0.4–66)	0.9(0.5–4.9)	0.9(nd–4.1)	0.7(0.4–4.9)	0.9(0.4–9.0)	1.15±0.04	12.6±3.2
BDE206	2.9(0.9–235)	2.5(0.5–76)	3.7(0.5–13)	1.7(0.2–21)	0.3(0.1–1.6)	0.4(nd–1.0)	0.3(0.1–2.3)	0.4(0.1–4.4)	1.22±0.08	12.8±3.5
BDE209	22(2.0–1836)	18(3.2–1012)	25(2.7–109)	14(0.7–233)	2.8(1.4–18)	3.9(1.2–13)	2.1(1.2–37)	3.2(1.7–93)	9.69±0.04	192±32
∑PBDE	66(8.0–4381)	41(6.1–7897)	53(5.7–198)	28(1.5–392)	6.6(3.0–33)	8.5(1.9–23)	3.9(2.4–51)	6.3(3.5–134)	13.7±1.5	275±40

STD: standard deviation; nd: not detected.

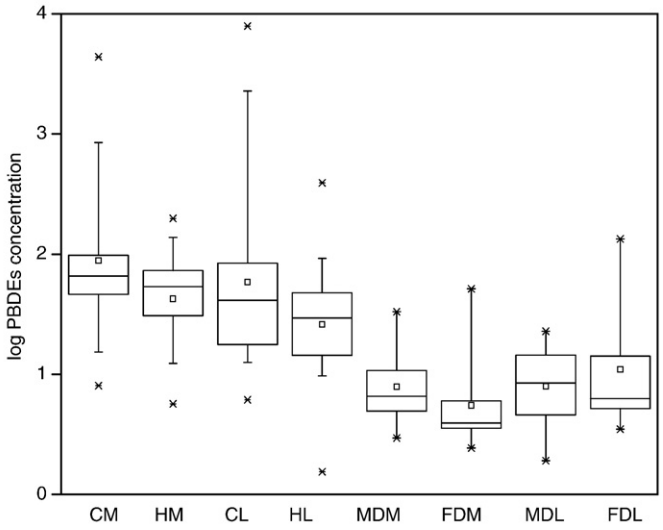

Fig. 1. Concentrations of PBDE in muscle and liver tissues for chicken and duck. CM: cock muscle, HM: hen muscle, CL: cock liver, HL: hen liver, MDM: male duck muscle, FDM: female duck muscle, MDL: male duck liver, FDL: female duck liver.

variation of selected compound concentrations. Limits of quantification (LOQ) were calculated based on a signal-to noise ratio of 3. LOQs for the analyzed compounds ranged between 17 and 367 pg/g lipid.

3. Result and discussion

3.1. Level of PBDEs in domestic fowl

The median concentrations and ranges for major PBDE congeners in muscle and liver for cocks, hens, female and male ducks are presented in Table 1. A large variability in PBDE concentrations was found between individual chickens. The concentration of PBDEs ranged from 5.7 to 4381 ng/g lipid and from 1.5 to 7897 ng/g lipid in muscle and liver of chicken, respectively. The highest concentration of PBDEs was measured in one cock liver. Of the 33 chickens analyzed, seven chickens (4 cocks and 3 hens) have PBDE concentrations exceeding 100 ng/g lipid in both the muscles and livers (Fig. 1). These chickens were found being purchased from farmers who live proximate to the e-waste dismantling workshops. In the present study, PBDEs in the surface soils collected from ground around these farmer's houses were detected with mean concentrations of 275 ng/g dry weight. This concentration was significantly higher than those in surface soils far away the dismantling workshops (less than 50 ng/g on averaged) in our pervious study (Luo et al., submitted for publication). Therefore, the elevated PBDE concentrations in chickens collected close to dismantling workshops were possibly attributed, in part, to the uptake of highly contaminated soils. The PBDE concentrations in muscle and liver of duck ranged from 2.4 to 51 ng/g lipid and from 1.9 to 134 ng/g lipid, respectively. These concentrations were significantly lower than those in chicken (Mann–Whitney *U* test, $P<0.001$).

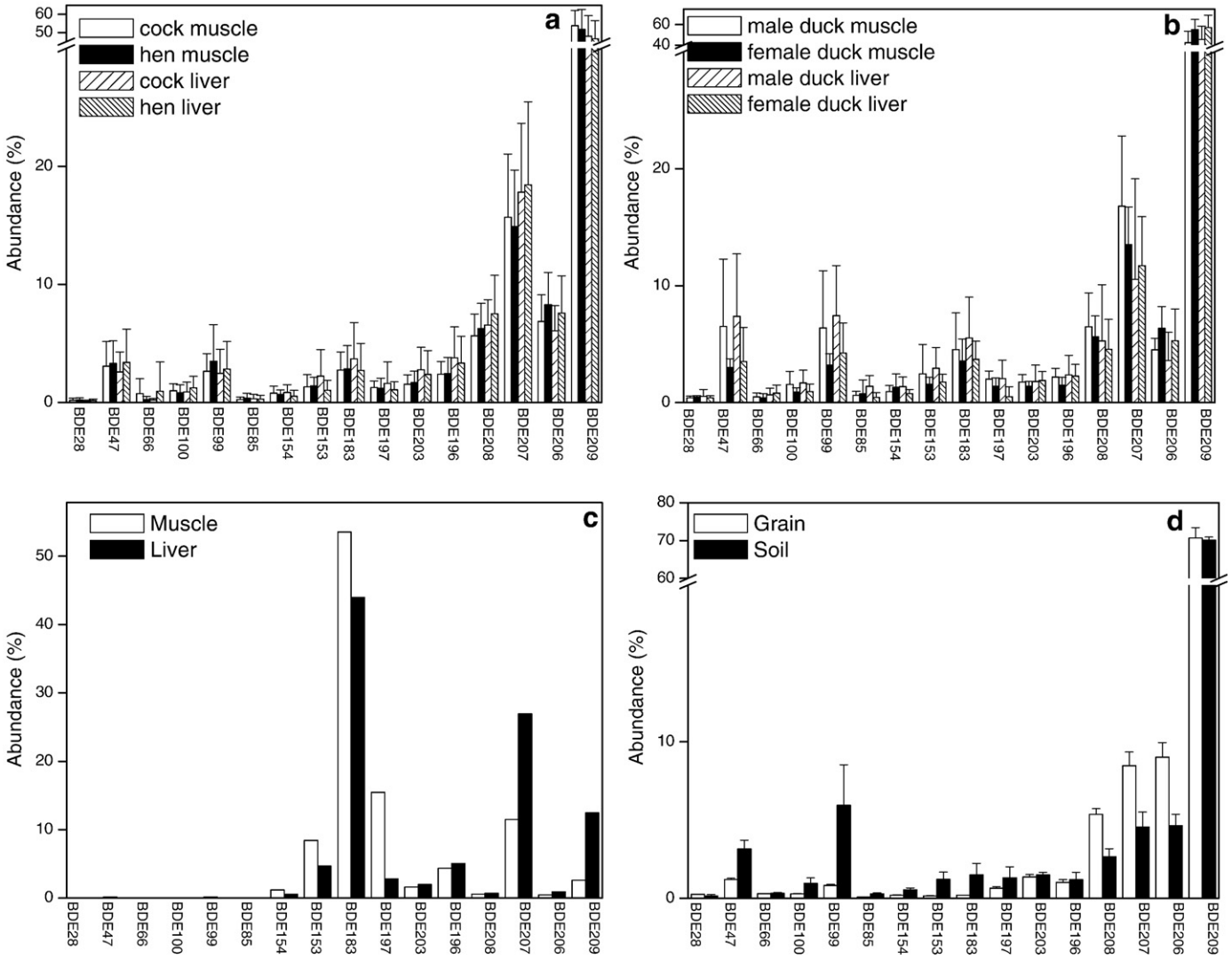

Fig. 2. Congener profile of PBDEs in chicken, duck, soil and grain collected from e-waste site. a: PBDE profiles in chicken excluding an exception of cock; b: PBDE profiles in duck; c: PBDE profiles in an individual cock; d: PBDE profile in grain and soil.

Grains are the most important food items for both chicken and duck. In the present study, PBDEs were detected at concentrations of 13.7±1.6 ng/g dry weight in three composite samples. One can expect that feeding grain is one of important exposure ways for poultry to PBDEs. However, the significant difference in PBDE concentrations between chicken and duck suggested that feeding grains might not be a major contribution to PBDEs burden in these poultry, especially for chicken. Other factors, such as living habitat and feeding habits, might play more important roles other than feeding grains on determination of PBDE burden in birds. Chicken is domesticated terrestrial bird. They roam and feed freely within a relatively large, yet confined, areas around the farmer's house. Besides grains, insects and domestic refuse were also important food items for chicken. While ducks spend their most time in water, and feed primarily on grains, vegetable shoots, insects, and surface feeder in ponds. Consequently, dietary uptake of more contaminated land-associated items (such as dusts and insects) likely contributed the relatively high PBDE burden in chicken. Additionally, the diverse rates of uptake, elimination, and metabolism between the two species can also contribute to the observed differences.

Unlike wild bird, few data exist on PBDE levels in poultry. Huwe et al. (2002) performed a study of PBDEs in chicken from the Southern US. In their study, mono- to deca-BDEs were detected at concentration of 1.8–39 ng/g in chicken fat samples, which fell in the low range of our study. Schecter et al. (2004) reported an upper concentration value of 0.28 ng/g wet wt. in chicken breast from market-based samples in Unite States. A study from Belgium reported that the levels of PBDEs in chicken breast were less than 0.031 ng/g wet wt (Voorspoels et al., 2007). The PBDE concentrations in chicken from Spanish commercial foodstuffs were reported lower than 0.117 ng/g wet wt. (Gómara et al., 2006). These values were significantly lower than the concentrations in the present study (0.15–74.8 ng/g wet wt. with medial of 1.38 ng/g wet wt.). Even though taking out account of nona- and deca-BDEs, the concentration of tri- to hepta-BDEs in the present study (0.02–8.0 ng/g wet wt with medial of 0.34 ng/g wet wt.) was still higher than those in above studies.

3.2. Sex and tissue distribution

Sex has been identified as an important factor on determination of the contaminant burden in biota (Hartmann et al., 2007; Burreau et al., 2006; Kenntner et al., 2003a). On one hand, females can reduce their body burden by transfer of contaminants into eggs (Newton et al., 1981; Tanabe et al., 1998); on the other hand, males have lower food conversion efficiency than females, which might also lead to the high contaminant body burden in males (Burreau et al., 2006). As shown in Fig. 1 and Table 1, the medial PBDE concentrations in muscle and liver tissues of males were slightly higher than those of females for both chicken and duck. However, this difference could not be proven to be statistical significance (Mann–Whitney U test, $P>0.05$). The lack of significant differences in PBDE concentrations between males and females in the present study could attribute to the relative shorter life-time for investigated birds. The net transfer of PBDEs by the egg-laying for females is limited because the birds collected in this study were less than one year old. No sex-related differences in contaminant concentrations have previously been found in some wild bird species by other studies (Cleemann et al., 2000; Kenntner et al., 2003b; Lundstedt-Enkel et al., 2005). It was suggested that there is another excretion route, the preen gland secretion, for lipophilic contaminants for birds. The preen gland secretion for contaminants exclusive for birds is more important than the egg-laying, and thus extinguish eventual the discrepancy in contaminant concentrations between female and male (Lundstedt-Enkel et al., 2005).

The PBDE concentrations in muscle were significantly higher than those in liver for chicken ($P=0.034$ for cock and $P=0.043$ for hen). This result is consistent with laboratory exposure (Van den Steen et al., 2007) and field (Voorspoels et al., 2006a) studies, which both reported that the PBDE concentrations in muscle were higher than those in liver for birds. The relatively higher metabolic activity in liver than in muscle is probably responsible for the higher concentrations in muscle compared to the liver (Voet and Voet 1995). For duck samples, the PBDE concentrations in muscle and liver were no statistically different ($P=0.92$ for male and $P=0.34$ for female). The relative low concentrations of PBDEs in ducks and the small sample sizes may mask any differences between tissues for duck.

3.3. Congener profile

With one exception of the cock, the PBDE congener profiles did not differ much between chicken and duck (Fig. 2a–c). Deca-BDE (BDE209) was the most abundant congener followed by nona-BDEs (BDE207, 206, and 208). Their sum collectively accounted for 78–82% and 70–81% of the total PBDE concentrations in chicken and duck, respectively. BDE47and 99, two major congeners of penta-BDE technical mixtures, contributed between 5.1% and 6.8% and between 6.2% and 15% to the total PBDEs in chicken and duck, respectively (Fig. 2a,b). BDE183, the major congener of octa-BDE technical mixtures, represented between 2.7% and 3.7% and between 3.6% and 5.5% of the total PBDEs in chicken and duck, respectively (Fig. 2a,b). These patterns found in the present study reflect that the deca-BDE technical product was the major source of PBDEs in this region. This is consistent with the fact that deca-BDE is mainly used in plastics, such as wire and cable insulation, TVs, computers and all other electrical and electronic equipment (Hale et al., 2002). These electrical and electronic equipments are major components of the e-wastes by handling in this studied site. Recently, more and more evidences have shown that higher brominated BDEs may accumulate in terrestrial food webs, including birds (Chen et al., 2007; Christensen et al., 2005; Dye et al., 2007; Jaspers et al., 2006; Kunisue et al., 2008a; Lindberg et al., 2004; Voorspoels et al., 2006a). The relatively higher contributions of BDE209 compared to other congeners have been observed in some Chinese terrestrial birds (buzzards, scops owls, and long-eared owls) and Japanese inland avian species (jungle crow), which attributed to the larger amounts of deca-BDE products used and produced in Asia relative to penta- and octa-BDE products (Chen et al., 2007; Kunisue et al., 2008a). Some terrestrial mammals, such as grizzly bears, red foxes, and raccoon dogs, were also dominated by the higher brominated BDEs in three previous reports (Christensen et al., 2005; Kunisue et al., 2008b; Voorspoels et al., 2006b). In those studies, BDE209 contributed more than 70% to the total PBDEs. Although exposure routes are unclear, it is suggested that the higher abundance of BDE209 in terrestrial mammals may be attributed to the intake of food contaminated with soil or atmospheric particles, in which BDE209 prevails. Furthermore, substantially high BDE209 concentrations (up to 3100 ng/g lipid) were found in blood of occupationally exposed populations (such as electronics-dismantling and rubber-manufacturing workers), where BDE209 was generally the major congener followed by nona- and octa-BDEs (Bi et al., 2007; Thuresson et al., 2005). Inhalation of particle-bound BDE-209 dust was an important exposure route for occupational workers. Therefore, the observed higher levels and higher contributions of BDE209 in domestic birds in the present study may be, at least partly, due to dietary and/or inhalational uptake of contaminated particulate matter (such as soils and dusts). Additionally, the feeding food (grain) is supposed to be also externally contaminated with particles as indicated by their similar congener profiles (Fig. 2d), and may represent another important source of BDE209 exposure for these domestic birds.

One individual cock shows a quite different congener profile from other chickens and ducks, in which BDE183 was the major congener, then followed by BDE207, 197 and 209 (Fig. 2c). The contributions of less brominated congeners, from BDE28 to BDE100, to total PBDEs concentration can be ignored. In a parallel study of dust near the dismantling workshop reveal that BDE183 have relatively high contribution (larger than 10%) to total PBDE concentrations in some road dust samples (Luo et al., submitted for publication). Therefore, exposure to the technical octa-mix for this individual cock might be one possible explanation for its different congener pattern.

Despite the PBDE profiles in biota samples, as a whole, were similar to the environmental matrix, some differences in PBDE profiles between environmental matrix and birds can be observed. First, the percentages of BDE209 (<60%) in birds were lower than those in grains and soils (70%). Second, the patterns of nona-BDE congeners in birds were different from those in grains and soils. In birds, the relative abundances of BDE207 were significantly higher than that of BDE206 and BDE208 ($P<0.05$), while in grain and soil samples, no significant difference exists among the abundances of BDE207, BDE206 and BDE208 (Fig. 2). The reason for these differences was likely due to the metabolic debromination of BDE209 in biota. A study of the anaerobic debromination of PBDE conducted by Gerecke et al. (2005) suggested that the favored BDE structure for microbial anaerobic debromination had bromine at meta- and para-positions. BDE207 had a bromine-free meta-position. Therefore, direct debromination of BDE209 at meta position might be one important pathway for BDE207 in biota. Several previous laboratory exposure studies on debromination of BDE209 in biota, such as rat, bird (*Sturnus vulgaris*) and cow, revealed that BDE207 was the major congener of nona-BDE (Kierkegaard et al., 2007; Huwe and Smith, 2007; Van den Steen et al., 2007) . Therefore, the difference in PBDE profiles between birds and environmental matrix pointed that the metabolic debromination of BDE209 might occurs in biota (Stapleton et al., 2006). However, other explanations, such as selective uptake and/or metabolism of the individual nonas or other input sources, can not been rule out in the present study.

ANOVA-analysis was performed to determine differences in PBDE profiles between species and between tissues and sexes in each species. Specific differences in the contributions of the different PBDE congeners between species could be observed in the present study (Fig. 2a, b). Generally, ducks have relatively higher contributions of the low brominated BDEs compared to chickens. The BDE47 and BDE99 together represented 6.2–15% of total PBDEs in ducks, while they accounted for 5.1–6.8% of total PBDEs in chickens. This finding could also be explained by different living habitats for these species. The ducks feeding in ponds may be more exposed to the lighter brominated BDEs by eating some aquatic species (such as small fish and shrimp) than chickens feeding on land. In fact, BDE47 and BDE99 were the major congeners in most aquatic birds, which have been demonstrated by many other studies (Elliott et al., 2005; Jaspers et al., 2005; Jaspers et al., 2006; Lam et al., 2007; Law et al., 2003). There was no significant difference in PBDE congener profiles between liver and muscle of the same species. Jaspers et al. (2006), who have measured the PBDEs profiles in different species of aquatic and terrestrial birds of prey in Belgium, have drawn the same conclusion. No significant differences were found between the profiles of liver and muscle from the same species. In analogy to that study are results from studies on birds of prey from the same region with similar PBDE congener profiles in various tissues (brain, adipose, liver, muscle and serum) for a certain species (Voorspoels et al., 2006a). However, marked interspecies discrepancies in PBDE profiles were observed in both studies. These observations were in concordance with our results for chicken and duck. Significant difference in the PBDE profiles between sexes was found for duck. The relative abundances of BDE47 and BDE99 were higher in male than those in female, but BDE209 was reverse. Two possible explanations can be given for this observation. First, BDE47 and BDE99 in female duck might be removed through egg-laying, which will lead to low burden in female duck. Second, difference in metabolic capacity between male and female duck could also result in this phenomenon. This sex-related difference in PBDE profiles was not found in chicken, which is most probably related to the overall lower contributions and concentrations of BDE47 and BDE99 in this species.

3.4. Assessment of human exposure through the consumption of poultry products

Chicken and duck are among the most consumed meat by the general population of China. More specially, chicken is the favorite food item for residents in Guangdong province as indicated by the slang that "never call it a feast without chicken". According to a report from Ministry of Agriculture of the Peoples Republic of China (MAPRC), the average per capita chicken consumption value was 1.43 kg/month in 2006 for residents in Guangdong ,which was three times of those for general Chinese population (0.394 kg/ month) (MAPRC, 2006). Therefore, PBDEs exposure from poultry consumption for residents in Guangdong, especially in e-waste sites should not be ignored. Using the PBDEs data from the present study (based on wet weight) and the per capital chicken and duck consumption values (47.7 g/day and 18 g/day, respectively) for residents in Guangdong province, reported by MAPRC (MAPRC, 2006), we calculated the PBDE intake per day for a local resident. The daily intakes of PBDEs through chicken and duck consumption ranged from 7.8 ng to 3582 ng with a medial value of 67.8 ng. The medial value (67.8 ng/day) in this study is 10 times higher than that from intakes of fish consumption in a recent survey for 13 commonly consumed fish species collected in Guangdong province (5.4 ng/day) (Meng et al., 2007). In the currently available publications on the issues of dietary PBDE intake, the calculated exposure levels ranged from 35 to 97 ng/day and varied geographically (Voorspoels et al., 2007). Considering these available data reported on the dietary PBDE intake did not include the high brominated congeners, we removed the deca-formulation-derived congeners (BDE206, 207, 208 and 209) for the calculation. The daily intakes of PBDEs were 1.3 to 384 ng with a medial 16 ng in this study, which was slight lower than other studies. However, it should be mentioned that above reported data were calculated based on various items of food products, while only poultry were considered in our assessment. Thus, the actual PBDEs intakes could be considerably enhanced if taking account of all other food products. Advice regarding consumption of locally produced food in the e-waste sites should be given to the local residents to protect their health. Further studies are suggested to assess the impact of pollutants on the local wildlife and human population.

4. Conclusion

The study offers data on the status of contamination of PBDEs in free-range fowls (chicken and duck), grains and surface soils collected from an e-waste recycling site in South China. As was shown by this study, the concentrations of PBDEs in chicken were much higher than those in duck, which could be attributed to different living habitat and feeding habits. No significantly sex-related differences in contaminant concentrations have been found for both species, confirming the assumption that there were more important contaminant exclusive routes for birds beside egg-laying. No difference could be seen in the PBDE congener patters between muscle and liver within the same species, while duck was found to accumulate more low brominated congeners than chicken. BDE209 and nona-BDEs were the major congeners in both fowls and environmental matrix in the present study. This suggests that biota samples in the study site were mainly exposed to the deca-BDE technical products. The daily dietary intake of PBDEs via consumption of locally food products is of great concern for residents lived in the e-waste sites.

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