Persistent Halogenated Compounds in Waterbirds from an e-Waste Recycling Region in South China

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Persistent halogenated compounds (PHCs), such as dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexane isomers (HCHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), decabromodiphenylethane (DBDPE), and polybrominated biphenyl 153 (PBB 153), were quantified in muscles of five waterbird species collected from an extensive e-waste recycling region in the Pearl River Delta, South China. PCBs, at concentrations up to 1,400,000 ng/g lipid, were the dominant contaminants contributing to 80%—90% of PHCs. PBDEs and organochlorine pesticides (sum of DDTs and HCHs) contributed approximately equally to total PHCs with median concentrations ranging from 37—2200 and 530—4300 ng/g lipid, respectively. This contaminant distribution pattern was different from those acquired by most studies conducted in other regions. The concentrations of PCBs and PBDEs in Chinese-pond heron from the present study were higher than those from most other previous studies with birds having similar trophic levels. The extensive e-waste recycling activities were probably the cause of the elevated PCB and PBDE levels in the bird samples. The median concentrations of PBB 153 and DBDPE ranged from 3—140 and 10—176 ng/g lipid, respectively. The frequent detection and high concentrations of DBDPE in piscivorous birds implicate a potential environmental concern for this "new" brominated flame retardant. Additionally, the interspecies differences in the levels of contaminants and species-specific PBDE congener patterns were also elucidated in the present study.

Introduction

Persistent halogenated compounds (PHCs), such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), are well-known for their persistency, bioaccumulation potential in organisms, and adverse effects on wildlife and human health. Dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs) are two typical classes of OCPs that have been widely used as insecticides. PCBs were historically used in a variety of products as dielectric and hydraulic fluids and were banned in the 1970s. PCBs continue to be released from a wide range of industrial activities particularly via the disposal of electrical waste. PBDEs are widely used as additive flame retardant in paints, textiles, and electronics. There is increasing regulation and phasing-out of production of the commercial usage of penta- and octa-BDE technical mixtures due to their potential toxicity to the environment and humans (*1*). As a replacement for BDE 209, decabromodiphenylethane (DBDPE) has been used in applications similar to those of the deca-BDE technical mixture. However, a few studies have reported the occurrence of DBDPE in the environment (*2*−*5*). Rising global demands for DBDPE undoubtedly will result in increasing DBDPE contamination in the future. There is thus a heightened concern regarding the environmental fate of and human exposure to DBDPE.

The Pearl River Delta (PRD), a coastal region of South China, has experienced accelerated environmental deterioration in the last three decades due to rapid industrialization and urbanization. High levels of DDTs and HCHs have been detected in water and sediments of the PRD, and new sources of DDTs may be present (*6*). PBDEs have also been widely detected in air, sediments, and biota from the PRD and an increased trend of PBDEs was recorded in sediment cores (*7, 8*). Making things worse, extensive e-waste recycling practices have emerged during the past decade in the PRD, accelerating the release of large amounts of toxic chemicals, including PBDEs and PCBs, into the environment. Several recent studies reported that the environment and humans at e-waste recycling sites were extensively contaminated with PBDEs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (*9, 10*). In addition, the e-waste recycling centers have become hot spots for PHCs. The possible adverse effect of pollutants from these hot spots on local wildlife and residents has been a significant concern. Unfortunately, little information on pollutants in wildlife is available so far.

Birds, both terrestrial and aquatic, have been used intensively as sentinel species for monitoring the levels and effects of PHCs in the environments because they are widespread and sensitive to environmental changes, and occupy the top position in the food chain (*11, 12*). In Europe and North America, a large number of studies have been conducted on PHCs contamination in avian species (*13*−*17*). However, only meager investigations have been performed on PHCs in avian species inhabiting China (*18*). Recently, Lam et al. (*19*) and Chen et al. (*20*) reported occurrence of PBDEs in eggs of waterbirds from the coastal area off South China and in tissues of birds of prey from North China. On the other hand, no data are available regarding the occurrence of PHCs (except for PBDEs) in birds from China, especially from e-waste recycling regions.

In the present study, various waterbird species from an extensive e-waste recycling region were collected and analyzed for PHCs. The objective was to elucidate the levels, patterns, and sources of PHCs in bird species from South China. The bioaccumulation patterns of PHCs in these bird species were also investigated. Additionally, recent studies have addressed that the fully brominated BDE congener (BDE 209) can bioaccumulate in terrestrial wildlife (*20*). Hereby, special emphasis was also placed on DBDPE because its chemical structure is similar to that of BDE 209 and is the second most currently used additive BFR in China, with domestic production of 12 000 t in 2006, next to that of the Deca-BDE mixture (20 000 t) (*21*).

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TABLE 1. Orgnohalogen Compound Levels (ng/g lw) in Muscle of Waterbird Species from the Pearl River Delta

compound	white-breasted waterhen ($n = 11$) *Amaurornis phoenicurus* median	range	slaty-breasted rail ($n = 5$) *Gallirallus striatus* median	range	ruddy-breasted crake ($n = 5$) *Porzana fusca* median	range	chinese-pond heron ($n = 5$) *Ardeola bacchus* media	range	common snipe ($n = 3$) *Gallinago gallinago* median	range
HCHs[b]	210	78−4200	460	150−630	150	55−420	1800	80−2800	190	39−840
DDTs[c]	460	81−3700	510	190−640	410	74−1500	2700	120−6900	330	73−3400
∑OCPs[d]	600	260−4900	960	510−1300	550	130−1800	4500	200−8700	530	110−4300
∑PCBs[e]	18000	2500−1400000	10000	4000−12000	1800	960−11000	120000	4300−270000	11000	8400−35000
∑PBDEs[f]	600	150−14000	820	130−1400	37	23−130	2200	530−2500	340	270−1700
DBDPE	13	nd[a]−220	22	5−62	10	4−16	180	33−800	96	29−110
PBB153	140	nd−2800	55	nd−94	10	2−39	3	1−86	43	6−530

[a] nd: not detected. [b] Sum of β-HCH, γ-HCH, and δ-HCH. [c] Sum of *p,p*′-DDT, *p,p*′-DDE, and *p,p*′-DDD. [d] Sum of HCHs and DDTs. [e] Sum of CB 28/31, 52, 60, 66, 74, 85, 90, 92, 99, 101, 105, 107, 110, 114, 115/87, 117, 118, 119, 123, 128, 130, 137, 138, 141, 146, 147, 149/139, 153, 154, 158, 164/163, 166, 167, 171, 174, 175, 177, 178, 180, 183, 187, 190, 191, 194, 195, 202, 205, 206, 207, 208, 209. [f] Sum of BDE28, 47, 100, 99, 154, 153, 183, 203, 196, 208, 207, 206, 209.

Materials and Methods

Field Sampling. Specimens ($n = 29$) from five bird species, including Rallidae (white-breasted waterhen, *Amaurornis phoenicurus*; $n = 11$; slaty-breasted rail, *Gallirallus striatus*; $n = 5$; ruddy-breasted crake, *Porzana fusca*; $n = 5$); Ardeidae (Chinese-pond heron, *Ardeola bacchus*; $n = 5$); and Scolopacidae families (common snipe, *Gallinago gallinago*; $n = 3$), were collected between 2005 and 2007 from Qingyuan County, the second largest e-waste recycling region in the PRD. Detailed information about the sampling site is provided in the Supporting Information. All birds collected were found dead or dying from various causes (traumas, poisoning, hunting, and distress, etc.), and the details are summarized in Table S1 of the Supporting Information ("S" designates tables or figures in the Supporting Information hereafter). Immediately after collection, birds were transported to the laboratory and those that could not be rescued were euthanized. Various tissues were excised and stored at −20 °C until chemical analysis. Pectoral muscle was used in the present study.

Sample Preparation. The procedure for sample extraction was detailed in a previous study (*22*). Approximately 2−6 g of muscle tissue was homogenized with anhydrous sodium sulfate, spiked with surrogate standards, $^{13}C_{12}$−BDE 209, CDE 99, and ^{13}C-PCB 141 for PBDEs, and PCB 65 and PCB 204 for PCBs and OCPs, and Soxhlet extracted with 50% acetone in hexane for 48 h. The lipid content was determined gravimetrically from an aliquot of the extract. Another aliquot of the extract used for chemical analysis was subject to gel permeation chromatography for lipid removal. The lipid-free eluate was concentrated to 2 mL and further purified on 2-g silica gel solid-phase extraction columns (Isolute, International Sorbent Technology, UK). The fraction containing organohalogen compounds was concentrated to near dryness and redissolved in 100 μL of isooctane. Known amounts of internal standards (^{13}C-PCB 208, BDE 118, and BDE 128 for PBDEs and PCB 24, 82, and 189 for PCBs and OCPs) were added to all extracts prior to instrumental analysis.

Chemical Analysis. The instrumental conditions, quantitation procedures, and quality assurance/quality control (QA/QC) measures and outcome are provided in the Supporting Information.

Data Analysis. All concentrations were lipid-normalized. ∑OCPs, ∑PCBs, and ∑PBDEs are defined as the sum of HCHs and DDTs, the sum of 51 PCB congeners, and the sum of 13 BDE congeners, respectively (Table S2). One-way analysis of variance (ANOVA) tests accompanied by Tukey's tests were used to evaluate the interspecies variability of contaminant levels and PCB homologue profiles. Principal component analysis (PCA) was performed using SSPS 11.5 to investigate the correlative relationships between pollutants and species.

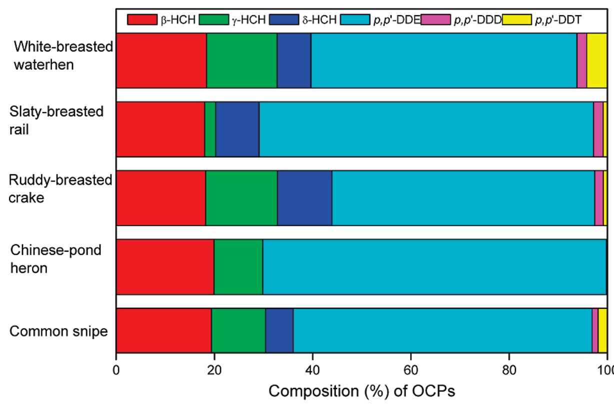

FIGURE 1. Composition (%) of OCPs in muscles of five bird species.

Results and Discussion

Levels and Profiles of Contaminants. Descriptive statistics for the levels of HCHs, DDTs, ∑OCPs, ∑PCBs, ∑PBDEs, BDPE, and PBB 153 are summarized in Table 1. The concentrations of individual PCB and PBDE congeners, DBDPE, PBB 153, and OCPs in each bird are provided in Table S2.

Among OCPs analyzed, DDTs were the most prevalent contaminants (Figure 1 and Table S1). *p,p*'-DDE was the most frequently detected (in all the samples) and its concentrations (ranging from 62−6900 ng/g) were higher than those of other OCP compounds (Figure 1). This result is consistent with those from several previous studies (*23*−*25*). *p, p*'-DDD was detected in 52% of the samples with a concentration range of 6−83 ng/g. The detectable frequency of *p, p*'-DDT was 24% with concentrations from 6 to 120 ng/g. β-HCH was also detected in all the samples with concentrations ranging from 30 to 1800 ng/g (Table S1). γ-HCH and δ-HCH were detected in 97% and 62% of the sample with the concentration ranges of 21−320 and 33−1000 ng/g, respectively. α-HCH was not detected in any samples. The frequent occurrence of *p, p*'-DDE and β-HCH at high levels along with the low detectable frequency of *p, p*'-DDT and complete absence of α-HCH suggest that OCP residues in the samples were largely derived from historical discharge instead of recent inputs.

The levels of PCBs ranged from 960 to 1,400,000 ng/g (Table 1). The highest concentration was found in one white-breasted waterhen and proved to be an outlier (Dixon's test, $p < 0.05$). As previously reported by Dauwe et al. (*16*), Naso et al. (*24*), and Frank et al. (*26*), the penta-, hexa-, and hepta-PCBs were predominant, constituting more than 80% of the ∑PCBs in all species (Figure 2). Of the PCB congeners mentioned above, the concentrations of PCB 153, 138, 180,

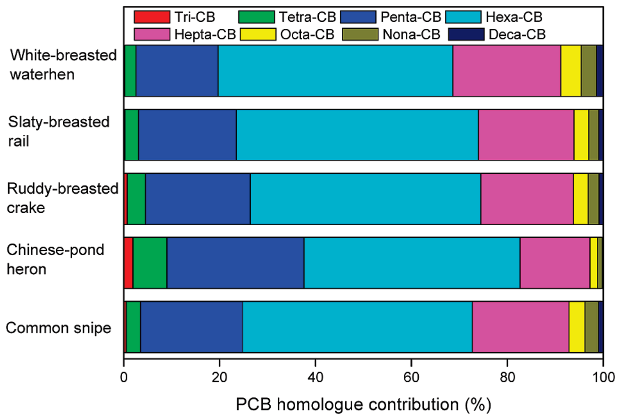

FIGURE 2. PCB homologue profiles in muscle of five bird species. Tri-CB: CB 28/31; Tetra-CB: CB 52, 60, 66, 74; Penta-CB: CB 85, 90, 92, 99, 101, 105, 107, 110, 114, 115/87, 117, 118, 119, 123; Hexa-CB: CB 128, 130, 137, 138, 141, 146, 147, 149/139, 153, 154, 158, 164/163, 166, 167; Hepta-CB: CB 171, 174, 175, 177, 178, 180, 183, 187, 190, 191; Octa-CB: CB 194, 195, 202, 205; Nona-CB: CB 206, 207, 208; Deca-CB: CB209.

and 118 collectively constituted 38−56% of the total ∑PCBs concentrations (Figure S1). These congeners are known to be highly recalcitrant because they all have unsubstituted adjacent *meta* and *para* positions on the biphenyl rings (*27*). The PCB homologue profiles in Chinese-pond heron were significantly different from those in white-breasted waterhen and slaty-breasted rail (ANOVA, $p < 0.05$) with elevated relative abundances of tri-, tetra-, and penta-PCBs (Figure 2). Different living habitats and feeding habits for the species might be responsible for this observation (more discussions follow).

The median concentrations of the sum of 13 PBDE congeners in five bird species ranged from 37 to 2200 ng/g. BDE 47, 99, 100, 153, 154, and 183 were detected in all the samples, and BDE 28 and 209 were detected in less than 50% of the samples (28% and 41%, respectively). Previous studies documented that BDE 47 was the dominant congener in aquatic birds, followed by BDE 99 (*13, 28, 29*), whereas terrestrial birds often contained BDE 99 and/or BDE 153 as the major components (*14, 15*). In the present study, PCA was conducted on the fractional composition of BDE congeners among birds to evaluate the species-specific congener profiles of PBDEs (Figure 3). The biplot of PCA reveals that the Chinese-pond heron and ruddy-breasted crake were enriched with BDE 47, 99, and 100, which was similar to the previously acquired results for aquatic birds (*14, 29*). On the other hand, white-breasted waterhen and common snipe tended to be enriched with BDE 153, 183, and 154. Pronounced accumulation of BDE 153 was also observed in pectoral muscle of some avian species (*20, 30, 31*) and in peregrine falcon eggs (*15, 32, 33*). Drouillard et at (*27*). found that BDE 47 had the lowest retention factor among tetra-hepta-BDE congeners, but BDE 153 was most persistent in the American kestrel. Therefore, the higher proportion of BDE 153 observed in birds might be related to different metabolic abilities of different species for PBDEs. The score point of slaty-breasted rail is located outside those of others species, indicating a significantly different congener profile (Figure 3). In slaty-breasted rail, BDE 209 was the predominant congener, followed by BDE 153, and the relative abundances of nona-BDE congeners were higher than those in other species (Figure S2). This congener pattern has been reported in some species of bird of prey from North China (*20*) and jungle crow from Japan (*30*). Recently, Gauthier et al. (*17*) reported that BDE 209 was a proportionally important BDE congener in herring gull eggs. Terrestrial sources of PBDEs are suspected to dictate the levels of BDE 209. Direct

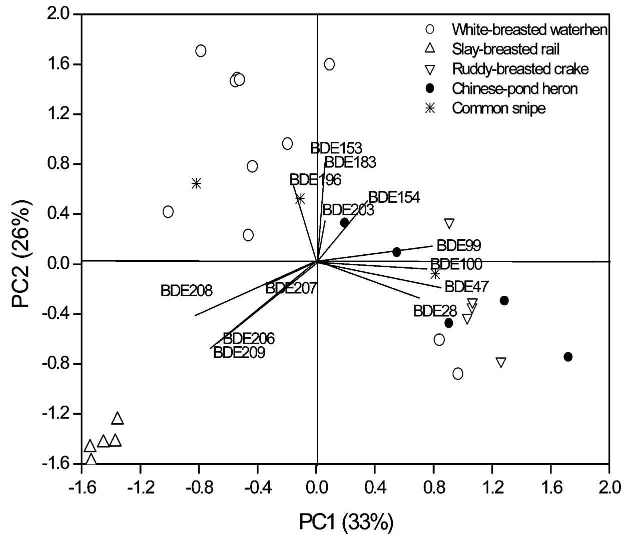

FIGURE 3. Biplot from principal component analysis based on the fractional compositional of BDE congeners (PC1, 33% variance; PC2, 26% variance). The full line originating from the center of the plot represents the factor loadings and the figure legends represent the factor scores for all birds analyzed.

exposure to Deca-BDE mixture and/or via the food chain by consuming insects that come in contact with BDE 209 containing materials at e-waste dumping sites might be the main reason for the high proportion of BDE 209 in slaty-breasted rail. Furthermore, debromination of BDE 209 might be largely responsible for the abundant levels of nona-BDE congeners in this species because biotransformation from BDE 209 to nona-BDE congeners has been reported in the European staring (*Sturnus vulgaris*) (*34*). Another significant finding regarding the BDE congener profiles in the present study is the high proportion of BDE 183, constituting 8%−16% of the total PBDE burden, in all species except for slaty-breasted rail. This indicates high levels of technical octa-BDEs in the study area.

DBDPE was detected in all samples except for one white-breasted waterhen with concentrations of 4−800 ng/g, which were 1 order of magnitude lower than those of BDE 209 in the samples containing detectable DBDPE and BDE 209 (Table S2). This may be attributed to the large difference between the quantities of BDE 209 and DBDPE used commercially, as the commercial use of DBDPE began in the 1990s, 20 years later than that of BDE 209. On the other hand, the frequent detection of DBDPE in bird samples and its relative high concentrations, up to several hundreds parts-per-billion, in Chinese-pond heron implied that DBDPE appeared to be more bioavailable for aquatic biota than BDE 209 since a high proportion of BDE 209 was usually found in terrestrial biota. Law et al. (*3*) also found that DBDPE was biomagnified in an aquatic food web with the trophic magnification factor being up to 9.2. Therefore, the environmental behavior of DBDPE may be different from that of BDE 209 although the chemical structures and physical−chemical characteristics of DBDPE and BDE209 are similar. Thus, more studies concerning DBDPE are needed to better understand its transformation, uptake, and toxicological effects on wildlife.

The occurrence of PBBs has not yet been reported in the environment of China. In the present study, PBB 153, a major compound of hexa-BB technical mixture, was detected in 93% of the samples with concentrations ranging 1−2800 ng/g. The levels of PBB153 were similar to those of the major PBDE congeners found in the samples except for Chinese-pond heron in which PBB 153 was significantly less abundant than PBDE congeners (Table S2).

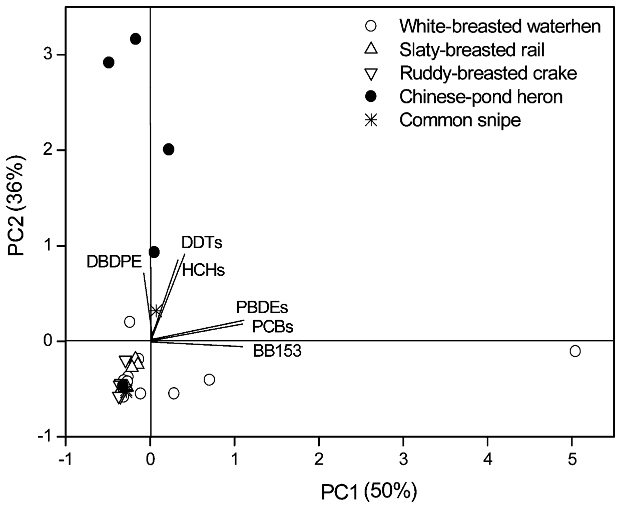

FIGURE 4. Principal component analysis biplot of the factor loadings (full line originating from the center of the plot) and factor scores, Concentrations of HCHs (sum of α-, *β*-, *γ*-, and *δ*-HCH), DDTs (sum of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT), PCBs (sum of CB28/31, 52, 60, 66, 74, 85, 90, 92, 99, 101, 105, 107, 110, 114, 115/87, 117, 118, 119, 123, 128, 130, 137, 138, 141, 146, 147, 149/139, 153, 154, 158, 164/163, 166, 167, 171, 174, 175, 177, 178, 180, 183, 187, 190, 191, 194, 195, 202, 205, 206, 207, 208, and 209), PBDEs (sum of BDE28, 47,100, 99, 154, 153, 183, 203, 196, 208, 207, 206, and 209), DBDPE, and BB153 were used to run PCA.

Geographical and Interspecies Comparison. It is difficult to compare data from different studies because of the difference in bird species sampled, tissues analyzed, the number of PCB or PBDE congeners targeted, and how the concentrations are expressed (i.e., lipid weight, wet weight, etc.). Because most previous publications focused on exposure of fish-eating birds and raptors to PHCs, only the data with Chinese-pond heron were used to compare with those in other studies (Table S3). The concentrations of PBDEs in Chinese-pond heron were higher than those in muscles and eggs of fish-eating birds from Asia and Europe (*19, 30, 31, 35, 36*), but lower than or comparable to those in fish-eating bird eggs from the Great Lakes (*13*) and British Columbia (*29*) (Table S3). The concentrations of PCBs in Chinese-pond heron were comparable to those in muscle of seabirds and piscivorous birds from Japan and Belgium (*30, 31*), but higher than those in waterbird eggs and tissues from Korea (*23*), the coastal areas of Campania, Italy (*24*), the Baltic Sea (*35*), and the Canadian Arctic (*37*), implying heavier PCB pollution in our study area. Regarding agrochemical pollution, DDTs concentrations in Chinese-pond heron were comparable to or lower than most reported values from other studies, while the levels of HCHs from the present study were higher than those from others studies (Table S3). The levels of PBB 153 in Chinese-pond heron were in the same order of magnitude as those found in fulmar muscle from Faroe Islands (*38*) and raptor muscles and eggs from Belgium (*11, 39*), and lower than those in peregrine falcon eggs from Sweden (*15*). In general, the concentrations of PCBs and PBDEs from the present study were at the high end of the worldwide range, while those of DDTs and PBB 153 were consistent with the commonly observed values in birds from around the world.

The correlation between the contaminant concentrations and bird species was evaluated by ANOVA, and post hoc comparisons were assessed by Tukey's tests. An outlier, associated with a white-breasted waterhen containing the highest levels of all target analytes, was removed before ANOVA. No significant difference in the mean concentration of PBB 153 was found among five species. The DBDPE level was significantly greater in the Chinese-pond heron than in other four species, and the levels of ∑PCBs and ∑OCPs were also significantly higher in Chinese-pond heron than in three rallidae family species. Finally, the concentrations of ∑PBDEs were significantly lower in the ruddy-breasted crake than in Chinese-pond heron.

Many factors, including dietary exposure, metabolic capability, migration pattern, age, sex, and nutritional state, can influence the levels of organic contaminants in birds (*31, 40–42*). In the present study, different feeding habits can be used to explain the observed interspecies difference (Table S1). Chinese-pond heron is a piscivorous bird feeding primarily on fish (95%) and aquatic insects. It is at the highest trophic level among all bird species investigated in the present study. Common snipe mainly feeds on 70% of larval insects and 30% of aquatic invertebrates in wetland areas. Slaty-breasted rail mostly feeds on shrimps, crabs, and insects. White-breasted waterhen is an insectivore/granivore generally feeding on insects, worms (about 80%), marsh plant shoots, paddy grains (15%), and fish (5%). The ruddy-breasted crake is an omnivore, sitting low in the food chain with diets comprising 55% of tender shoots and berries, 35% of aquatic insects, and 10% of mollusks (*43*). These different diet compositions partly explain why high concentrations of PHCs were obtained in Chinese-pond heron but low levels were found in ruddy-breasted crake. Previous studies (*24, 44*) also reported that the levels of PHCs were higher in piscivores birds than in omnivores, insectivores, and granivores. Although the species-specific differences in diet are discussed in the present study, it is impossible to quantify the impact of dietary factors on the pectoral muscle concentration in these birds without obtaining the PHCs levels in dietary items. Due to the lack of data or limited sample number, other factors, such as migration pattern, sex, metabolic capability, were not further investigated in the present study.

Contaminant Pattern and Sources. PCBs were the dominating contaminants in all birds, accounting for 81% to 92% of total PHCs (Figure S3). The contribution of PBDEs to total PHCs was approximately equivalent to that of OCPs for each species except for ruddy-breasted crake which contained more OCPs than PBDEs (17% vs 2%). The contribution of PBB 153 or DBDPE to total PHCs was less than 1% in all species. This distribution pattern was different from that in birds of prey from northern China, where *p,p'*-DDE constituted the largest portion of PHCs (*44*). This pattern was also different from those reported in other regions. For example, the concentrations of OCPs were higher than or comparable to those of PCBs in birds from Korea (*23*), Europe (*12, 25*), North America (*38, 46, 47*), and South Africa (*48*). In addition, concentrations of PBDEs in birds were lower than those of OCPs from some previous studies (*16, 35, 36, 38*). The contaminant distribution pattern from the present study indicates that industrial sources are more important than agrochemical sources in the study area. Elevated PCB and PBDE levels in the analyzed birds appear to have resulted from the extensive e-waste recycling activities in the study area. In our previous study, very high PCB and PBDE levels were found in surface soils near e-waste workshops and in biota samples from an e-waste polluted reservoir in the study area (*48, 49*), confirming the above hypothesis. The high relative abundance of OCPs in ruddy-breasted crake may be attributed to its migratory habit since it only stays in the study area in summer. Our recent analyses of biota samples collected from the Pearl River Estuary showed that OCPs were predominant PHCs in all the samples (unpublished data), consistent with most previously published results. This finding strongly implies that the predominance of PCBs in the bird samples from the present study was derived from the e-waste recycling activities. Obviously, more analyses of birds residing at non-e-waste sites are needed to confirm the above conclusion.

A PCA analysis was conducted on the concentrations of ∑DDTs, ∑HCHs, ∑PCBs, ∑PBDEs, DBDPE, and PBB 153 to demonstrate the relationship among variables (Figure 4). The Chinese-pond heron is separated from other bird species, indicating a different exposure route for this species, which has been demonstrated in the previous section. The different variables are clustered in three separate groups (Figure 4), i.e., PCBs, PBDEs, and PBB 153 are in one group, HCHs and DDTs are in another group, and DBDPE is in the third group. So far, no information is available regarding the use history of PBBs, but the strong correlation between PBB 153 and PCB/PBDEs found in the present study implied that e-waste might also be the major source of PBBs in the study area. As a traditional agriculture region, OCPs, such as HCHs and DDTs, were used in large quantities for agriculture and public health purposes until the official ban on the production and use of DDTs in 1983. Presumably, historical inputs should have been the major source of HCHs and DDTs, as also discussed above. As a separate group in the PCA plot, DBDPE may have a different source from other organohalogen compounds. Leaches from local commercial materials may be a main source of DBDPE found in the bird samples because DBDPE is the second highest current-use additive BFR and its consumption grows at a rate of 80% per year in China (*21*).

Acknowledgments

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Supporting Information Available

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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