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Halogenated organic pollutants in aquatic, amphibious, and terrestrial organisms from an e-waste site: Habitat-dependent accumulation and maternal transfer in watersnake☆

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ABSTRACT

Dichlorodiphenyltrichloroethanes (DDTs), Polychlorinated biphenyls (PCBs), and halogenated flame retardants (HFRs) were measured in aquatic, amphibious, and terrestrial wildlife collected from an e-waste contaminated pond and its surrounding region. The species-specific bioaccumulation and maternal transfer of chemicals in the watersnake were investigated. Total concentrations of target chemicals ranged from 1.3×10^3 to 4.8×10^5 ng g^{-1} lipid weight. PCBs were the predominant (72–95%) contaminants, followed by polybrominated biphenyl ethers (PBDEs, 4–27%). The concentrations of PCBs and HFRs except decabromodiphenyl ethane (DBDPE) were higher in aquatic organisms and terrestrial birds than in amphibians and lizards. Relatively high DDT levels were observed in the terrestrial birds and toads, but high DBDPE was found in the aquatic species except for waterbird eggs. Species-specific congeners profiles for PCB and PBDE and isomeric composition for dechlorane plus were observed. These results indicated a habitat-dependent accumulation among different species. Maternal transfer examined by the ratio of egg to carcass for watersnakes indicated multi-linear correlations between maternal transfer potential and octanol-water partition coefficient (log K_{OW}) of chemicals. The same maternal transfer efficiencies were found for chemicals with log K_{OW} between 6 and 8, then the maternal transfer potential rapidly decreased with increasing of log K_{OW}.

1. Introduction

Electronic waste (e-waste) is a critical global environmental health issue, especially in developing countries. As an important source of contaminant, e-waste can release halogenated organic pollutants (HOPs), including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dechlorane plus (DP), and other halogenated flame retardants, into the ambient environment by inappropriate disposal (Robinson, 2009; Zhang et al., 2012). These hazardous chemicals would then be accumulated by organisms from the environmental media and magnified along the food chain, owing to their persistence and bioaccumulation (Jepson and Law, 2016; Kelly et al., 2007). Presently, HOPs have been frequently detected in biota samples, including fish (Wu et al., 2008), insects (Nie et al., 2015), frogs (Wu et al., 2009a), and birds (Luo et al., 2009), from an e-waste recycling region in Longtang town in south China.

The accumulation of persistent organic pollutants was investigated in the diverse wildlife in the field (Malaj et al., 2014; Smith et al., 2007). Fish and invertebrates are primary indicators of pollution in aquatic ecosystems (Hu et al., 2010; Malaj et al., 2014; Zhang et al., 2010a), while birds (as predators) in terrestrial ecosystems (Peng et al., 2015; Sun et al., 2012a). Amphibians are also important organisms, owing to their sensitivity to environmental pollution in both aquatic and terrestrial habitats (Liu et al., 2011; Ter Schure et al., 2002; Wu et al., 2009a). Species-specific accumulations for HOPs were reported in previous studies. For example, Jaspers et al. (2006) reported that terrestrial birds accumulated higher brominated BDE congeners than aquatic birds from Flanders in Belgium. Similar results were also found between chicken eggs and goose eggs collected from an e-waste site in South China (Zeng

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et al., 2016). *Syn*-DP was found to preferentially accumulate in aquatic organisms, but this was not the case for terrestrial birds (Sun et al., 2012b; Zeng et al., 2016). However, few studies have provided a comprehensive investigation of bioaccumulation of HOPs in organisms among different habitats.

Reptiles, specifically lizards and snakes, are important components in many terrestrial and aquatic ecosystems, but they are often excluded from environmental contaminations studies (Campbell and Campbell, 2002). Because of their unique physiology and life history traits, predicting the accumulation characteristic of HOPs in reptiles via other vertebrates (e.g., birds and fish) is ineffective (Smith et al., 2007). Some species of snakes and lizards are ovoviviparous (Shine, 1983). Previous studies investigated the transfer of organohalogen pollutants from maternal tissues to the eggs in oviparous species (e.g., fish, birds, and frogs) (Nyholm et al., 2008; Peng et al., 2012; Van den Steen et al., 2009; Wu et al., 2009a) and to the offspring in viviparous species (e.g., surfperch and marine mammals) (Nakata et al., 1995; Oka et al., 2006). The results of these studies suggested the differences in the mechanism of maternal transfer regarding organic contaminants during reproduction. However, no knowledge is currently available on the maternal transfer of HOPs in ovoviviparous species.

E-waste recycling regions have been identified as hot spots for HOPs. In this study, a total of 10 wildlife species—including aquatic (fish, prawn, watersnake, and waterbird eggs), amphibious (frog and toad), and terrestrial (lizard and three terrestrial resident passerine birds) species—were collected from an extensive e-waste recycling site in South China. The carbon and nitrogen stable isotopes for all samples were measured to identify the food source and trophic position of organisms. The levels of HOPs, including PCBs, PBDEs, dichlorodiphenyltrichloroethanes (DDTs), DPs, decabromodiphenyl ethane (DBDPE), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), and polybrominated biphenyls (PBBs), were determined in all samples. The objective of this study was to investigate the accumulation patterns of HOPs among wildlife with different habitats and to examine the maternal transfer of HOPs in ovoviviparous species.

2. Materials and methods

2.1. Sampling

Samples were collected from a pond located in Longtang Town, Qingyuan County of Guangdong Province and the surrounding region (within a 500 m radius). The pond has been heavily polluted by chemicals associated with e-waste, as a large amount of unwanted e-waste was discarded in the pond. Details of the sample site were provided in a previous study (Wu et al., 2008). A total of 52 organism samples were collected between April and May 2016. The aquatic biota collected from the pond included: fish (Common carp, *Cyprinus carpio*, six pooled samples from 49 individuals); prawn (Oriental river prawn, *Macrobrachium nipponense*, five pooled samples from 79 individuals); waterbird egg (White-breasted waterhen, *Amaurornis phoenicurus*, $n = 6$), and watersnake (Chinese watersnake, *Enhydris chinensis*, $n = 7$). Watersnake eggs were found in three of the watersnakes. Toad (Black-spectacled toad, *Duttaphrynus melanostictus*, $n = 6$) and frog (Asiatic painted frog, *Kaloula pulchra*, 5 pooled samples from 9 individuals) were captured by the traps from the farmlands near the pond. The terrestrial biota was captured by the mist nets around the pond and included three resident passerine birds: Long-tailed shrike (*Lanius schach*, $n = 2$); Eurasian blackbird (*Turdus merula*, $n = 2$); Oriental magpie-robin (*Copsychus saularis*, $n = 3$), and one species of reptile: lizard (Oriental garden lizard, *Calotes versicolor*, $n = 10$). All samples were transported to the laboratory in an ice box and dissected after recording the length and mass of the body. The eggs, muscles, and carcasses of samples were freeze-dried, homogenized by a stainless-steel blender, and then stored at −20 °C until analysis.

2.2. Chemical analysis

Approximately 1 g of the freeze-dried sample (egg, muscle, or carcass) was mixed with ashed anhydrous sodium sulfate and spiked with surrogate standards (CB24, 82, and 198 for PCBs and DDTs; BDE118, BDE128, 4-F-BDE67, 3-F-BDE153 and ^{13}C-BDE209 for halogenated flame retardants). The samples were then soxhlet extracted with hexane/dichloromethane (1/1, v/v) for 48 h. An aliquot of each extract (10%) was removed for gravimetric lipid determination, while the remaining extract was prepared for gas chromatograph mass spectrometer analysis (GC/MS). Prior to instrumental analysis, the extract was spiked with known amounts of the recovery standards (CB30, 65, and 204; BDE77, 181, and 205). PCBs and DDTs were analyzed by Agilent GC/MS using electron ionization (EI) in a selected ion monitoring mode (SIM); PBDEs, DP, DBDPE, PBT, PBEB, HBB, and PBBs were analyzed by the electron capture negative ionization mode (ECNI). Detailed procedures of sample pretreatment, instrumental analysis, quality assurance, and quality controls are provided in the Supplementary Information (SI).

2.3. Stable isotope analysis

All samples for carbon isotope (δ^{13}C) and nitrogen isotope (δ^{15}N) analysis were freeze-dried and ground into powder. Approximately 0.5 mg of each sample was placed into a tin capsule and analyzed using a Flash EA 112 series elemental analyzer coupled with a Finnigan MAT ConFlo III isotope ratio mass spectrometer. Stable isotope abundances were calculated by the formula:

$$\delta^{13}X = (R_{sample}/R_{standard} - 1) \times 1000 \qquad [1]$$

Where X represents ^{15}N or ^{13}C, and $R_{sample}/R_{standard}$ is the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratio of the sample and reference standard (Vienna Pee Dee Belemnite for δ^{13}C and nitrogen for δ^{15}N). The precision for this technique is approximately ±0.5% (2 SD) for δ^{15}N and ±0.2% (2 SD) for δ^{13}C.

2.4. Statistical analysis

Statistical analyses were performed using SPSS 19.0 and Origin 8.5. Student *t*-test and One-way ANOVA was used to evaluate the interspecific differences in the isotope values and contaminant levels. Principal component analysis (PCA) was conducted to investigate the correlative relationships between the pollutants and species. Least squares linear regression analyses were used to test for relationships between the maternal transfer and physico-chemical properties of the organohalogen pollutants. Values were considered statistically significant when $p < 0.05$.

3. Results and discussion

3.1. Stable carbon and nitrogen isotopic signatures

Stable isotope analysis was used to elucidate the diet preferences and trophic levels of the consumers. Significant interspecific differences were observed for the δ^{13}C and δ^{15}N values (Fig. 1 and Table 1). Due to the small number of samples ($n = 2$) and large variation in δ^{13}C and δ^{15}N values, the data for the long-tailed shrike and Eurasian blackbird were presented individually rather than as a statistical value (mean) in Fig. 1 and Table 1.

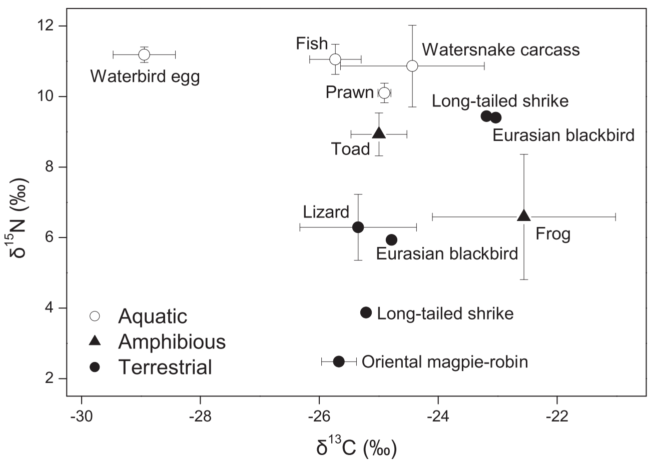

Fig. 1. Stable isotope ratios of C and N in aquatic, amphibious, and terrestrial species.

The $\delta^{13}C$ values of all organisms, except waterbird eggs, were within a relatively narrow range from −25.7‰ to −22.6‰ (Fig. 1), indicating that the aquatic and terrestrial predators had a similar carbon source. The $\delta^{13}C$ value of waterbird eggs (−28.9‰) were significantly lower than those of other species ($p < 0.01$). This can be explained by the difference in lipid contents. Ehrich et al. (2011) demonstrated that fatty tissues (eggs) have lower $\delta^{13}C$ values than lean tissues (muscles), as lipids contain less $\delta^{13}C$ than proteins do. In the present study, the lipid contents in waterbird eggs reached 11%, but in the tissues of other species were between 0.75 and 3.3% (Table 1).

The $\delta^{15}N$ values of aquatic species ranged from 10.1‰ to 11.2‰, and the values of amphibious and terrestrial species were range from 2.5‰ to 9.4‰ (Table 1). The $\delta^{15}N$ values for aquatic organisms and terrestrial birds were in the line of those for the same species in previous studies (Sun et al., 2012a; Wu et al., 2009b). The $\delta^{15}N$ values of aquatic species were significantly higher than those of amphibious and terrestrial species ($p < 0.05$) (Fig. 1), which may be explained by the difference in background $\delta^{15}N$ values between aquatic and terrestrial environments. The $\delta^{15}N$ values were much higher in aquatic plants than in terrestrial plants (Cloern et al., 2002; Goedkoop et al., 2006).

3.2. Concentrations of contaminants

The concentrations of ΣPCBs, ΣPBDEs, ΣDDTs, DP, DBDPE, and ΣOBFRs (OBFR = brominated flame retardants without PBDEs; sum of PBT, PBEB, HBB, PBB153, and PBB209) and the levels of individual PCB and PBDE congeners are provided in Table 1 and Tables S2 and S3.

The levels of DDTs were significantly higher in the terrestrial birds than in the aquatic organisms and the frogs ($p < 0.05$). The toads have comparable DDT concentrations with those in the

Table 1
Median concentrations and range of HOPs in aquatic, amphibious and terrestrial species (ng g-1 lw) from an e-waste recycling site.[a]

Species	Aquatic					Amphibious		Terrestrial			
	Fish	Prawn	Waterbird egg	Watersnake carcass	Watersnake egg	Frog	Toad	Lizard	Oriental magpie-robin	Eurasian blackbird	Long-tailed shrike
Length (cm)	3–5	2–4	3.5–4	44–65	0.5–0.8	2–5.5	7–8	22–40	18–19	26, 28	25, 26
Weight (g)	0.5–1	0.3–1	17–21	30–224	27–38	2–16	29–50	5–27	32–36	82, 105	44, 46
Lipid (%) [b]	1.2 ± 0.22	1.4 ± 0.07	11 ± 0.69	0.75 ± 0.22	14 ± 2.3	2.1 ± 0.80	3.3 ± 0.27	1.6 ± 0.63	0.88 ± 0.03	1.3, 1.3	1.5, 1.1
$\delta^{13}C$ (‰) [b]	−25.7 ± 0.43	−24.9 ± 0.11	−28.9 ± 0.52	−24.4 ± 1.2	−25.7 ± 1.2	−22.6 ± 1.5	−25.0 ± 0.47	−25.3 ± 0.98	−25.7 ± 0.29	−24.8, −23.0	−25.2, −23.2
$\delta^{15}N$ (‰) [b]	11.1 ± 0.43	10.1 ± 0.28	11.2 ± 0.22	10.9 ± 1.2	14.0 ± 0.57	6.6 ± 1.8	8.9 ± 0.61	6.3 ± 0.94	2.5 ± 0.09	5.9, 9.4	3.9, 9.4
ΣPCBs [c]	1.6×10^5 (1.0×10^5 -1.8×10^5)	6.3×10^4 (5.9×10^4 -6.9×10^4)	2.9×10^4 (2.8×10^4 -3.5×10^4)	5.3×10^4 (2.7×10^4 -4.5×10^5)	1.9×10^5 (1.4×10^5 -2.3×10^5)	5.6×10^3 (3.5×10^3 -1.1×10^4)	5.8×10^3 (3.1×10^3 -1.1×10^4)	1.5×10^3 (9.9×10^2 -1.1×10^4)	4.4×10^4 (2.8×10^4 -1.1×10^5)	1.6×10^4 3.4×10^4	4.0×10^4 2.8×10^5
ΣPBDEs [d]	1.2×10^4 (6.6×10^3 -1.6×10^4)	6.2×10^3 (4.8×10^3 -1.2×10^4)	2.7×10^3 (2.4×10^3 -2.8×10^3)	2.7×10^4 (1.2×10^4 -8.0×10^4)	5.5×10^3 (4.0×10^3 -8.2×10^3)	490 (310–1400)	260 (210–550)	200 (130–550)	1.2×10^4 (2.7×10^3 -1.3×10^4)	1.9×10^3 3.1×10^3	3.6×10^3 1.2×10^4
ΣDDTs [e]	450 (270–490)	280 (260–330)	250 (220–330)	410 (120–1700)	1000 (640–1200)	85 (24–470)	1000 (200–3200)	nd	2900 (2500–8500)	3000 1400	3300 3100
ΣDP [f]	570 (240–1200)	240 (140–640)	260 (150–350)	150 (77–610)	99 (65–240)	51 (29–150)	24 (16–60)	27 (6.4–70)	80 (73–620)	190 480	94 190
DBDPE	620 (440–1000)	340 (330–900)	nd [i]	680 (110–3800)	11 (9.9–12)	25 (8.9–72)	9.2 (7.5–19)	19 (6.5–56)	12 (4.3–14)	16 14	22 27
ΣOBFRs [g]	2400 (1200–3200)	300 (230–380)	160 (150–180)	110 (56–1300)	310 (240–540)	37 (18–180)	35 (14–70)	46 (25–130)	320 (240–1600)	130 160	510 3100
ΣHOPs [h]	1.7×10^5 (1.1×10^5 -2.0×10^5)	7.3×10^4 (6.7×10^4 -7.8×10^4)	3.2×10^4 (3.1×10^4 -3.8×10^4)	7.9×10^4 (3.9×10^4 -4.8×10^5)	1.9×10^5 (1.5×10^5 -2.4×10^5)	6.7×10^3 (4.2×10^3 -1.2×10^4)	8.0×10^3 (3.7×10^3 -1.4×10^4)	1.8×10^3 (1.3×10^3 -1.2×10^4)	5.0×10^4 (4.3×10^4 -1.3×10^5)	2.1×10^4 3.9×10^4	4.8×10^4 3.0×10^5

[a] Median (mix-max).
[b] Mean ± SD.
[c] Sum of 30 selected PCB congeners (CB18, 28/31, 49, 52, 74, 87/115, 95, 99, 101, 105, 110, 118, 128, 138, 146, 149, 153/132,156, 163/164, 167, 170/190, 174, 180/193, 183, 187, 189, 194, 196/203, 206 and 209).
[d] Sum of 17 PBDE congeners (BDE28, 47, 66, 99, 100, 138, 153, 154, 183, 196, 197, 202, 203, 206, 207, 208 and 209).
[e] Sum of *p,p*'-DDE; *p,p*'-DDD and *p,p*'-DDT.
[f] Sum of *syn*-DP and *anti*-DP.
[g] Sum of PBT, PBEB, HBB, PBB153 and PBB209.
[h] Sum of ΣPCBs, ΣPBDEs, ΣDP, DBDPE, ΣOBFRs, ΣDDTs.
[i] Not detectable.

terrestrial birds. However, no DDTs were detected in the lizards (Table 1). In a study on HOPs in insects in the same study region, we found that flying insects such as dragonflies, butterflies, and moths have significantly higher DDT levels than aquatic insects and jumping or crawling insects (Liu et al., 2018). The terrestrial birds proved to feed frequently upon the flying insects (Marshall, 1949), while the lizards preferred to feed upon the jumping and crawling insects such as orthopteran (Andrews et al., 1987). This is a possible explanation for the DDT distribution among the different organisms investigated in the present study. The DDT levels in the toads (1000 ng g^{-1} lw) were one order of magnitude higher than those in the frogs (85 ng g^{-1} lw) in the frogs. Similarly, the DDTs in the muscle tissues of Asiatic toads (680 ng g^{-1} lw) were higher thant that in dark-spotted frogs (61 ng g^{-1} lw) from the Yangtze River Delta (Zhou et al., 2016), indicating that toads accumulated more DDTs than did frogs.

The aquatic species exhibited slightly higher or comparable levels of ΣPCBs, ΣPBDEs, ΣOBFRs, and DP compared to the terrestrial birds, but significantly higher levels compared to those observed in the amphibians and lizards ($p < 0.05$) (Table 1). The highest concentrations of these chemicals were found in the fish from the pond, which was expected since the pond was heavily polluted by chemicals associated with e-waste (Luo et al., 2009; Wu et al., 2008). Unlike DDTs, the levels of ΣPCBs, ΣPBDEs, ΣOBFRs, and DP in the toads were similar to or lower than those in the frogs (Table 1). As mentioned above, DDT levels were higher in lepidopterans than in other insects in another study, but the concentrations of other chemicals in the lepidopterans were comparable with other insects (Liu et al., 2018). The observed difference between frog and toad in the present study may be explained by a greater proportion of lepidopterans in the diet of the toad than that of the frog, but this need more studies to confirm the feeding habits of the toads and frogs.

DBDPE was detected in all aquatic samples with the exception of the waterbird egg. The median concentrations of DBDPE in the fish, prawn, and watersnake carcasses were one to two orders of magnitude higher than those of the other organisms investigated in the present study (Table 1). The high DBDPE levels in these aquatic organisms could be attributed to these species having more chances to obtain DBDPE by the consumption of particles contaminated by DBDPE in the pond. High concentrations of DBDPE were previously reported in the sediment of this pond (Wu et al., 2010a). No DBDPE was detected in the waterbird egg, which could be due to the lower efficiency of maternal transfer of DBDPE. The observed DBDPE levels in the watersnake carcass were two to three orders magnitude higher than those in the watersnake egg (Table 1). The same case might also be found in the waterbird. Unlike PCBs, PBDEs, and OBFRs, the levels of DBDPE in terrestrial birds were noticeably lower than that in aquatic species, which implied that the accumulative potential of DBDPE may be weaker than other organic pollutants in the terrestrial birds.

3.3. Composition patterns of contaminants

PCBs were the predominant contaminants in all species studied, accounting for 72–95% of total HOPs investigated (Fig. 2). PBDEs were the second most abundant contaminants with contributions ranging from 4 to 27% of total HOPs. The highest and the lowest abundance of PBDEs were observed in the watersnake carcass and watersnake egg, respectively. This was due to the less efficient maternal transfer of PBDEs than PCBs in watersnake, which is discussed in greater detail in the next section. The proportions of DDTs were higher in the three terrestrial bird species (6.2%) and two amphibian species (3% in the frog and 14% in the toad) than in the other species (less than 1%). As discussed above, a diet with a high proportion of lepidopteran might explain this observation. DDTs were generally the dominant contaminants among HOPs in the wildlife of this region without point-source (Meng et al., 2007; Peng et al., 2015). The contaminant patterns of organisms in the present study indicated that industrial contaminants overwhelm agricultural contaminants in the study area due to the e-waste recovery activities.

PCB118, 138, 153, and 180 were the most abundant congeners in all species (except for fish), and their concentrations collectively constituted 46–64% of the total PCBs concentration (Figure S1). PCA using fraction composition of PCB congener was conducted to evaluate the habitat-dependent accumulation of PCBs in aquatic, amphibious, and terrestrial species (Fig. 3). The lizard and fish samples are clustered on the top and left of the score plot, respectively, and are separated from other samples. The lizard samples exhibit a high abundance in high-chlorinated congeners, whereas the fish samples present a high abundance in low-chlorinated congeners (Fig. 3). Waterbird egg, prawn, and water-snake carcasses are clustered together with high abundance for moderate-chlorinated congeners. Frog and terrestrial bird overlap with each other, and toad was between the terrestrial bird and aquatic wildlife in the score plot. Previous studies demonstrated that the contributions of tri- and tetra-PCBs to total PCBs were higher in fish and prawns than in watersnakes and waterbirds (Luo et al., 2009; Wu et al., 2008). Moreover, hetpa- and octa-PCBs have a relatively higher bioaccumulation potential in terrestrial birds (Drouillard et al., 2001), which is consistent with the results in the present study. The interspecific difference in the PCB congener profile among wildlife could be attributed to differences in feeding habits and metabolism.

Regarding PBDEs, BDE209 was the predominant congener in all samples except for terrestrial birds, and the highest abundance was 79% in watersnake carcasses (Fig. 4). The highest contribution of BDE209 in watersnake carcass was due to the less efficient maternal transfer of BDE209, which is discussed in more detail in the following section. The contribution of BDE47 was noticeably higher in fish and prawns than in amphibious and terrestrial species (Fig. 4). The latter showed a relatively high proportion of high-brominated congeners (primarily BDE153 and 183). Previous studies reported that BDE47 was the dominant congener in aquatic species, followed by BDE99 (Hu et al., 2010; Xia et al., 2008), whereas terrestrial species often preferentially accumulated BDE153 and/or BDE209 (Peng et al., 2015; Voorspoels et al., 2006). For amphibians, the predominance of BDE99 and 153 was observed in frogs and was intermediate between aquatic and terrestrial wildlife (Liu et al., 2011; Wu et al., 2009a), which is consistent with the results of the present study. Additionally, the high proportion of BDE183 and 197, constituting 15–40% of the total PBDE burden in the amphibious and terrestrial species, indicated high levels of technical octa-BDEs in this study area.

The isomer composition of DP, described by f_{anti} (level of *anti*-DP divided by the sum of *syn*-DP and *anti*-DP) showed the highest value in the oriental magpie-robin (0.81) and the lowest in the watersnake carcasses (0.55) (Tables S2 and S3). The soil in the farmland and the water in the pond had mean f_{anti} values of 0.76 and 0.79, respectively, which were similar to the reported values in the DP commercial product ($f_{anti} = 0.75–0.80$)(Wang et al., 2016). Compared with these values, the oriental magpie-robin exhibited an *anti*-DP preferential enrichment, while other species showed some degree of *syn*-DP preferential accumulation. Generally, f_{anti} in terrestrial organisms was higher than that in aquatic organisms, with the exception of prawns (Figure S2). In a study on DP in domestic fowl, Zeng et al. (2016) also found that the terrestrial domestic fowl (chicken) exhibited higher f_{anti} than the aquatic domestic fowl (goose). These results indicated that different

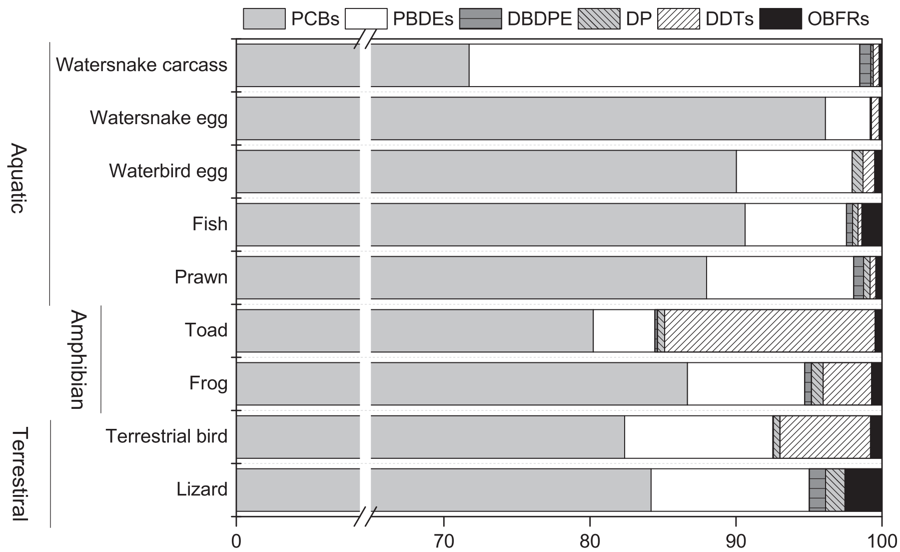

Fig. 2. Contaminant compositions of HOPs in aquatic, amphibious, and terrestrial species.

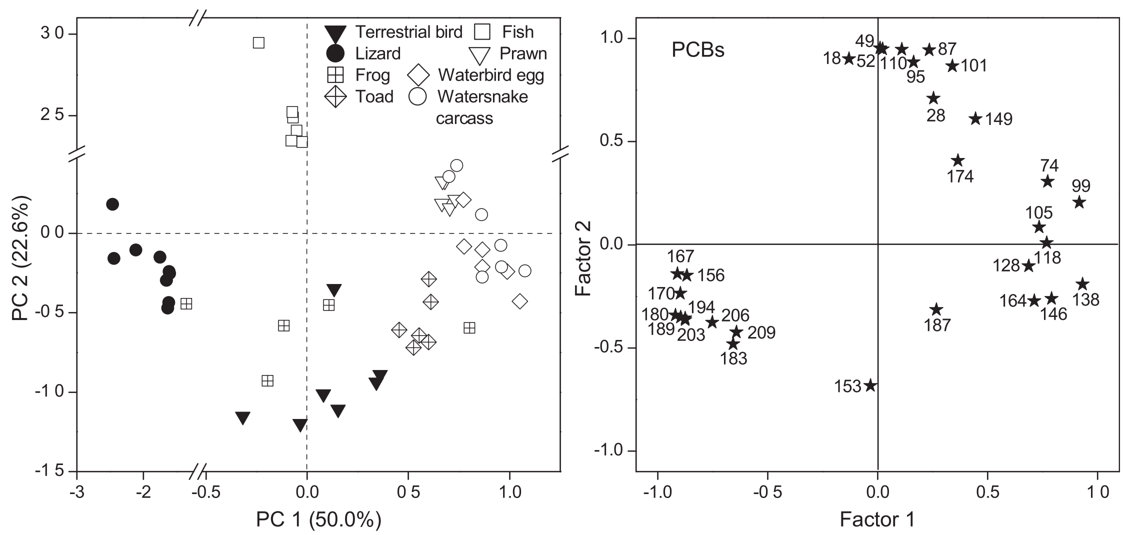

Fig. 3. Score plot for PCA of PCBs in aquatic, amphibious, and terrestrial species.

isomer-selective bioaccumulation of DP does occur between aquatic and terrestrial organisms. Previous studies found that the f_{anti} was negatively correlated with the trophic level of organisms in both terrestrial and aquatic food webs (Tomy et al., 2007; Wu et al., 2010b). Significant negative correlations were also found between f_{anti} values and $\delta^{15}N$ in both aquatic and terrestrial organisms (Figure S2). The reason for this decline in f_{anti} remains unknown, and more studies are therefore necessary.

3.4. Maternal transfer in watersnake

Watersnake is an ovoviviparous species. Embryonic development occurs in the maternal body and takes 2–3 months. Fertilized eggs stay in the maternal body longer than do ova or fertilized eggs in oviparous organisms (e.g., fish, birds, and frogs) (Shine, 1983; Walker and Tait, 2004). However, during development, embryos do not obtain nutrients from the maternal body. Thus, the maternal transfer of contaminants during egg formation determined the levels of pollutants in the egg.

The average levels of PCBs, PBDEs, DDTs, DP, DBDPE, and OBFRs in watersnake egg were 1.9×10^5, 5.5×10^3, 1000, 99, 11, and 310 ng g^{-1} lw, respectively (Tables 1 and S2). The levels of PCBs, DDTs, OBFRs in the egg were significantly higher than those in the corresponding maternal body (PCBs: 5.3×10^4, DDTs: 410, OBFRs: 110 ng g^{-1} lw), whereas levels of PBDEs, DP, and DBDPE were significantly lower than those in the corresponding maternal body (PBDEs: 2.0×10^4; DP: 150; DBDPE: 610 ng g^{-1} lw) ($p < 0.01$). Meanwhile, the congener profiles of PBDEs in the egg also differed significantly from those in the maternal body. BDE209 was the predominant congener in the maternal body, accounting for 79% of total PBDEs. However, its abundance decreased to 7.2% in the egg. On the contrary, the abundances of BDE47, 100, 154, and 153 increased sharply (Fig. 5). Regarding PCBs, most congeners with fewer than six Cl substitutions exhibited decrease in the abundance but congeners with larger than six Cl substitutions exhibited increase in the abundance, although no significance was observed ($p > 0.05$) (Figure S3).

The alternations in contaminant composition and congener

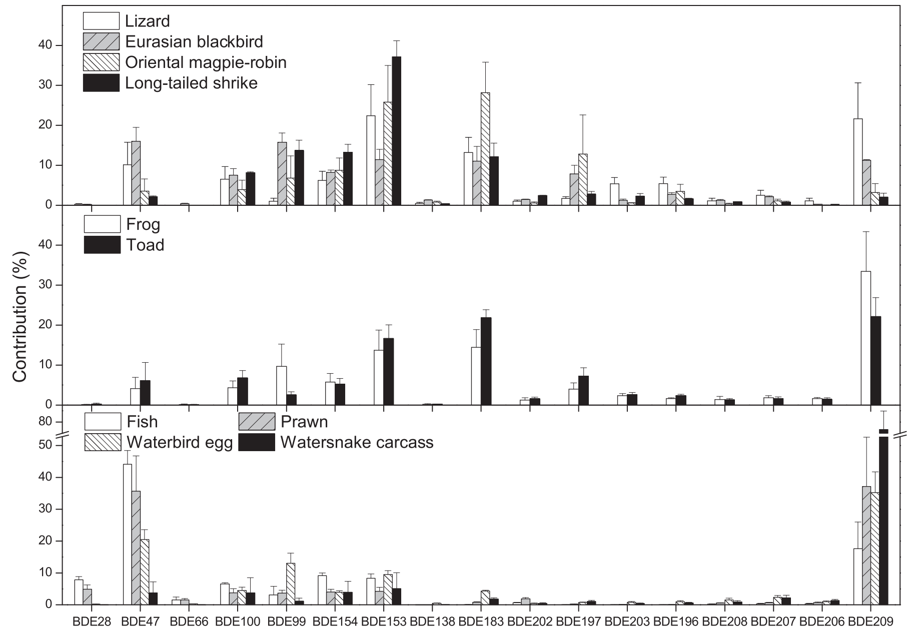

Fig. 4. Congener profiles of PBDEs in aquatic, amphibious, and terrestrial species.

profiles of PBDEs and PCBs in egg could contribute to the maternal transfer of contaminants. To fully elucidate the maternal transfer of contaminants in the watersnake, the mass ratio of egg to carcass plus egg (ECER) and the lipid-normalized concentration ratio of egg to carcass (ECR_L) were calculated using the following equations (Oka et al., 2006; Russell et al., 1999), respectively:

$$ECER\ (\%) = C_{egg} \times M_{egg}\ /\ (C_{carcass} \times M_{carcass} + C_{egg} \times M_{egg}) \quad [2]$$

$$ECR_L = C_{egg}/C_{carcass} \quad [3]$$

where C_{egg}, $C_{carcass}$, M_{egg}, and $M_{carcass}$ in Eq. (2) were concentrations on wet weight basis in egg and carcass and wet weight of egg and carcass. C_{egg} and $C_{carcass}$ in formula 3 were concentrations on lipid weight basis in egg and carcass.

Egg accounted for 27% of the total wet weight of the watersnake (carcass + egg). However, only the percentages of BDE209 and DBDPE in the egg were less than 27% (17% and 10%, respectively), and the majority of contaminants are larger than 80% (Fig. 6 and Table S4), which implied that most of the contaminants are preferentially deposited in the eggs. Lipid content is a major but not sole cause for this observation. The lipid content in the watersnake eggs was 14 ± 2.3%—nearly 20 times that in the watersnake carcass (0.72 ± 0.08%). However, the ECR_Ls were larger than one for all contaminants except for hepta-to deca-BDE congeners, *syn*- and *anti*-DP, DBDPE, and PBB209 (Table S4). The ECR_L being larger than one indicated more readily maternal transferred for chemicals during egg formation. The difference in lipid composition between egg and carcass might explain this occurrence. The lipids in the egg may have a higher abundance of neutral lipids, such as triglyceride and cholesterol ester, but a lower abundance of polar lipids such as

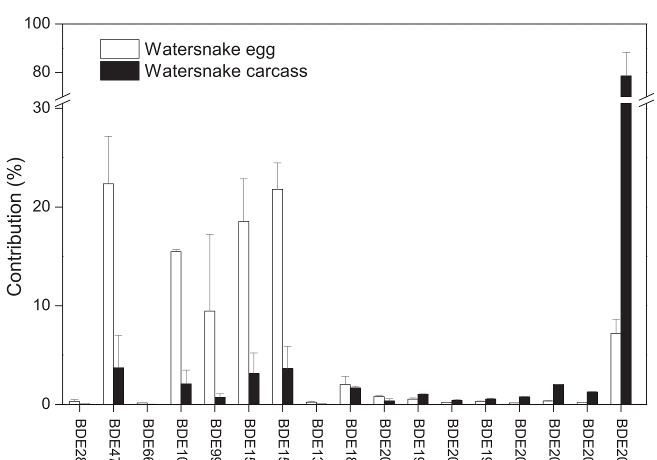

Fig. 5. Congener profiles of PBDEs in eggs and carcasses of watersnake.

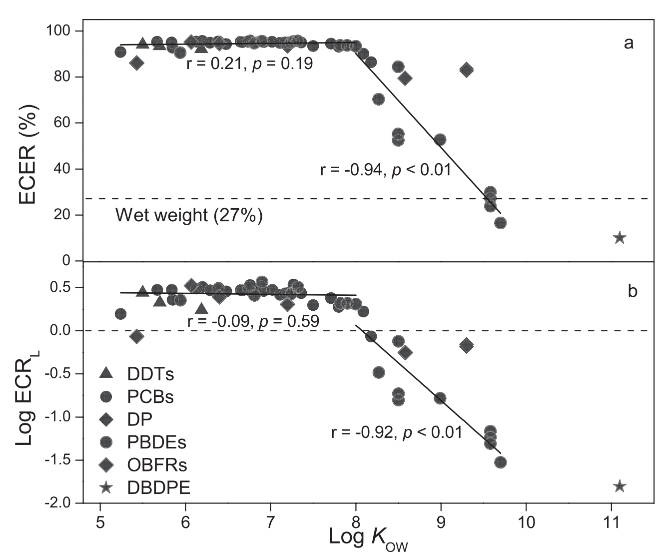

Fig. 6. Relationship between ECER (a) and log ECR_L (b) and log K_{OW} for HOPs in watersnakes. The dash lines in (a) represent the rates of lipid weight or wet weight in egg to carcass + egg. Log K_{OW} values were taken from Hawker and Connell, 1988) (Hawker and Connell, 1988); Choi et al., 2009 (Choi et al., 2009); Zhang et al., 2010 (Zhang et al., 2010b); and Covaci et al., 2011 (Covaci et al., 2011).

phospholipid and free cholesterol. The ECR_Ls of hepta-to deca-BDE, *syn*- and *anti*-DP, DBDPE, and PBB209 were less than one, which could be attributed to their lower potential to permeate the cell membrane due to their large steric hindrance. It was unexpected for the ECR_L of PBT to be less than one, and this might be due to the larger uncertainty of data due to the lower concentrations in the eggs and carcasses.

A correlation analysis revealed a multi-linear relationship between the maternal transfer potential of chemicals and the octanol-water partition coefficient (log K_{OW}) of chemicals. For chemicals with low hydrophobicity (log K_{OW}<6), the maternal transfer potential seems positively correlated to the log K_{OW} (Fig. 6). However, a confident conclusion cannot be drawn due to the small data points in the present study. The chemicals with log K_{OW} between six and eight exhibited the same maternal transfer potential, and a platform was found for plots of ECR_L and log K_{OW} as well as ECER and log K_{OW}. When log K_{OW} of chemicals was larger than eight, a negative relationship between the maternal transfer potential and log K_{OW} was observed.

The maternal transfer of chemicals in the watersnake clearly differs from those in other species reported in previous literature. A significant negative correlation between EMR and log K_{OW} (from 5 to 10) of polybrominated compounds was found in Chinese sturgeon (Peng et al., 2012; Zhang et al., 2010a). In contrast, a strong positive correlation between EMR and log K_{OW} (from 3 to 15) was observed in European eels (Sühring et al., 2015). Van den Steen et al. (2009) found that the bioaccumulative and persistent PCB congeners (e.g., CB118, 138, 153, 180, and 183) were more readily transferred from maternal tissues to the egg in blue tits. Similar results were reported in chicken by (Zheng et al., 2015). In a study on the maternal transfer of PBDEs in frog, Wu et al. (2009a) found that the ratio of egg to liver increased with increasing numbers of bromine atoms (up to seven) and then declined as bromine atom numbers further increased. However, Nyholm et al. (2008) reported that hydrophobic compounds (e.g., BDE183 and 209) are more efficiently transferred than less hydrophobic compounds (e.g., BDE28 and HBCDs) in zebrafish (*Danio rerio*). These results indicated potentially high interspecific differences in the maternal transfer of chemicals. Considering that embryos are more sensitive to chemical exposure than adults, more studies on the mechanism of maternal transfer for different species are necessary.

4. Conclusions

The present study demonstrated that the concentrations of PCBs and HFRs, except DBDPE, were significantly higher in the aquatic organisms and terrestrial birds than in the amphibians and lizards. Species-specific congener profiles for PCB and PBDE and isomeric composition for DP were also found among different organisms. These results indicated a habitat-dependent accumulation among different species. The congener profile of PBDEs in the watersnake egg was significantly differed from those in the maternal body. The same maternal transfer efficiencies were observed for the chemicals with log K_{OW} values between six and eight, and then the efficiency rapidly decreased as log K_{OW} increased until 11.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.06.038.

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