



## Occurrence and biomagnification of organohalogen pollutants in two terrestrial predatory food chains



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### HIGHLIGHTS

- Various classes of OHPs were determined in three Chinese raptors and their prey.
- Biomagnification potentials were assessed through the two predatory food chains.
- DDTs were the predominant pollutants followed by PBDEs, PCBs, HBCDs and DP.
- The relationships between log BMF and log  $K_{OW}$  followed a similar function.

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### ABSTRACT

Organohalogen pollutants (OHPs), including dichlorodiphenyl trichloroethane and its metabolites (DDTs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and dechlorane plus (DP), were determined in three raptor species, namely, the common kestrel (*Falco tinnunculus*), eagle owl (*Bubo bubo*), and little owl (*Athene noctua*), as well as in their primary prey items: Eurasian tree sparrow (*Passer montanus*) and brown rat (*Rattus norvegicus*). DDTs were the predominant pollutants in avian species followed by PBDEs and PCBs, then minimally contribution of HBCDs and DP. Inter-species differences in the PBDE congener profiles were observed between the owls and the common kestrels, with relatively high contributions of lower brominated congeners in the owls but highly brominated congeners in the kestrels. This result may partly be attributed to a possible greater *in vivo* biotransformation of highly brominated BDE congeners in owls than in kestrels.  $\alpha$ -HBCD was the predominant diastereoisomer with a preferential enrichment of (–)-enantiomer in all the samples. No stereoselective bioaccumulation was found for DP isomers in the investigated species. Biomagnification factor (BMF) values were generally higher in the rat–owl food chain than in the sparrow–kestrel food chain. Despite this food chain-specific biomagnification, the relationships between the log BMF and log  $K_{OW}$  of PCBs and PBDEs followed a similar function in the two food chains, except for BDE-47, -99, and -100 in the sparrow–kestrel feeding relationship.

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### 1. Introduction

Organohalogen pollutants (OHPs), such as dichlorodiphenyl trichloroethane and its metabolites (DDTs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and dechlorane plus (DP), are well known for their persistence, long-range transport, and potential toxicity to wildlife and humans (Alaee et al., 2003; Covaci et al., 2006; Sverko et al., 2011). Due to their top occupation in the food chains, birds of prey are extensively used as bioindicators of envi-

ronmental contamination (Chen and Hale, 2010). Previous studies have demonstrated that PBDEs behave differently in terrestrial vs. aquatic ecosystems. For instance, aquatic birds were usually BDE-47 accumulated, whereas the birds feeding entirely or partially on terrestrial-based food items had elevated abundance of BDE-153 or higher brominated congeners (Chen and Hale, 2010). Our previous study (Yu et al., 2011) also suggested the particular concern over the bioaccumulation and biomagnification of BDE-209 and its degradation products because of their possibly high ecological risks in terrestrial ecosystems. A study conducted in Belgium also showed indisputable biomagnification of PBDEs in two avian food chains (great tit–sparrowhawk and rodent–buzzard feeding relationships), whereas no biomagnification was found in the rodent–fox food chain (Voorspoels et al., 2007). Such food

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chain-dependent trophic transfer effect may indicate more complicated mechanisms of biomagnification in terrestrial ecosystems. Unfortunately, few studies have been devoted to the biomagnification potential of OHPs, especially HBCDs and DP, in terrestrial ecosystems (Covaci et al., 2006; Sverko et al., 2011; Sun et al., 2012; Xian et al., 2011). Even for legacy pollutants, such as PCBs and DDTs, data on terrestrial biomagnification is scarce.

In the present study, three species of birds of prey in Beijing, China, namely, the common kestrel (*Falco tinnunculus*), eagle owl (*Bubo bubo*), and little owl (*Athene noctua*), as well as their prey (sparrows and rats) were collected. These species were analyzed for various classes of OHPs, including DDTs, PCBs, PBDEs, HBCDs, and DP. The inter-species differences in OHP profiles of the terrestrial organisms were examined. Two predatory food chains were established to compare the biomagnification potentials of the various OHPs within different terrestrial food chains. This study also aimed to extend the database on emerging OHPs in terrestrial wildlife from China. It would contribute to further comprehensive biological risk assessments of OHPs in terrestrial ecosystems.

## 2. Materials and methods

### 2.1. Sampling

Birds of prey, including little owl ( $n = 14$ ), eagle owl ( $n = 10$ ) and common kestrel ( $n = 23$ ), were obtained from the Beijing Raptor Rescue Center between January 2005 and July 2007. The specimens received were either dead, died during rehabilitation, or euthanized because of serious injuries. Two prey species (Eurasian tree sparrow (*Passer montanus*,  $n = 40$ ) and brown rat (*Rattus norvegicus*,  $n = 8$ )) were captured in the locations where the raptors were collected. The common kestrels, sparrows, and rats used in this study had earlier been analyzed for PBDEs; the sampling information was introduced in detail in our previous publication (Yu et al., 2011).

The prey species were selected on the basis of their dominance in the diet compositions of the examined birds of prey. Sparrows account for 83% and 50% of the total prey items of common kestrels in Beijing area, according to direct observation and prey remains identification, respectively (Yu et al., 2011). Rodents, such as brown rats, form a vast majority (>90%) of owls' diet (Zhao et al., 2011).

### 2.2. Sample preparation and chemical analysis

The procedures for sample pretreatment in this study are similar to those employed in our previous study (Yu et al., 2011), with modest modifications as described in the Supplementary Data (Appendix A.2). Details of the instrumental conditions, quality assurance/quality control (QA/QC) measures and outcomes are provided in the Supplementary Data (Appendices A.3 and A.4).

### 2.3. Data analysis

The method detection limit (MDL) was defined as the mean value plus three times the standard deviation in procedural blanks ( $n = 10$ ). For analytes which cannot be detected in blanks, a signal-to-noise ratio of 10 was set as the corresponding MDL. Enantiomeric fractions (EFs) were calculated as the ratio of (+)-enantiomer over the sum of both enantiomers, of which peak areas were corrected in accordance with corresponding isotopic-labeled diastereomer standards (Marvin et al., 2007).

All concentration data were presented on a lipid weight (lw) basis.  $\Sigma$ PBDEs,  $\Sigma$ PCBs,  $\Sigma$ DP,  $\Sigma$ HBCDs, and  $\Sigma$ DDTs were defined as the sum of 16 BDE congeners, 37 PCB congeners, *anti*- and *syn*-DP, three HBCD diastereomers ( $\alpha$ -,  $\beta$ - and  $\gamma$ -), and *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT, respectively (Appendix A.1). Non-normally distributed data (determined by the Shapiro–Wilk test) were logarithmically transformed to normal distribution before being subjected to one-way ANOVA accompanied by LSD tests on SPSS 17.0. The level of significance through the present study was set at  $\alpha = 0.05$ .

## 3. Results and discussion

### 3.1. Contaminant levels and toxicological significance

Levels of  $\Sigma$ PBDEs,  $\Sigma$ HBCDs,  $\Sigma$ DP,  $\Sigma$ PCBs, and  $\Sigma$ DDTs in the investigated species are summarized in Table 1. No significant differences ( $t$ -test,  $p > 0.05$ ) in the concentrations of the studied OHPs were observed between the two owl species, and therefore data on the two owl species was combined and treated as one population. The median concentrations of total OHPs in the common kestrels (2100 ng g<sup>-1</sup> lw) and owls (15000 ng g<sup>-1</sup> lw) were 1–2 orders of magnitude higher than those in the sparrows (840 ng g<sup>-1</sup> lw) and rats (640 ng g<sup>-1</sup> lw). This is consistent with the fact that birds of prey have higher bioaccumulation potentials for organic contaminants than do the prey. Among the pollutants measured, DDTs

**Table 1**  
Median concentration (range) and bioaccumulation parameters of the investigated OHPs in the studied samples (ng g<sup>-1</sup> lw).

Species	CK <sup>a</sup> ( $n = 23$ )	Owl ( $n = 24$ )	ETS ( $n = 40$ )	BR ( $n = 8$ )
Lipid (%) <sup>b</sup>	12.2 ± 3.3	8.9 ± 4.8	10.4 ± 4.1	20.6 ± 10.2
$\Sigma$ PBDEs <sup>c</sup>	400 (120–8500)	580 (46–67000)	250 (100–2600)	150 (70–330)
$\Sigma$ HBCDs <sup>d</sup>	6.6 (nd <sup>i</sup> –260)	260 (18–440)	51 (6.5–1100)	17 (1.4–180)
$\Sigma$ DP <sup>e</sup>	1.5 (nd–60)	49 (7.0–500)	4.9 (nd–31)	24 (nd–160)
$\Sigma$ PCBs <sup>f</sup>	370 (44–17000)	1300 (190–71000)	59 (23–720)	42 (15–92)
$\Sigma$ DDTs <sup>g</sup>	1000 (120–110000)	12000 (610–1500000)	330 (89–11000)	140 (120–4000)
$\Sigma$ OHPs <sup>h</sup>	2100 (450–130000)	15000 (2000–1600000)	840 (240–13000)	640 (260–4100)
EF <sub><math>\alpha</math></sub> <sup>b</sup>	0.25 ± 0.09	0.29 ± 0.10	0.12 ± 0.05	0.29 ± 0.04
$f_{\text{anti}}$ <sup>b</sup>	0.79 ± 0.06	0.79 ± 0.12	0.75 ± 0.06	0.77 ± 0.11

<sup>a</sup> CK: common kestrel; Owl: including eagle owl and little owl; ETS: Eurasian tree sparrow; BR: brown rat.

<sup>b</sup> Mean ± SD.

<sup>c</sup> Sum of BDE-28, -47, -99, -100, -153, -154, -183, -196, -197, -201, -202, -203, -206, -207, -208, and -209.

<sup>d</sup> Sum of  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCD.

<sup>e</sup> Sum of *syn*-DP and *anti*-DP.

<sup>f</sup> Sum of PCB-28/31, -52, -60, -66/95, -74, -99, -105, -118, -128, -130, -137, -138, -146, -149/107, -153/132, -156, -158, -163, -167, -170/190, -178, -180/193, -183, -187, -191, -194, -203, -206, -207, -208 and -209.

<sup>g</sup> Sum of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT.

<sup>h</sup> Sum of  $\Sigma$ PBDEs,  $\Sigma$ HBCDs,  $\Sigma$ DP,  $\Sigma$ PCBs, and  $\Sigma$ DDTs.

<sup>i</sup> Not detectable or below the MDLs.

were the predominant compounds in the investigated birds of prey and sparrows, accounting for 46.0–82.0% of total OHPs. The contributions of PBDEs to total OHPs were equivalent to that of PCBs (6.7–35.4% vs. 7.7–22.8%), and those of HBCDs and DP were minimal (0.2–10.1%) in all the samples. The dominance of DDTs in total OHPs was also measured in birds collected from the Yellow River Delta, North China (Gao et al., 2009). The results of the aforementioned study differed from the findings on the peregrine falcon in Canada (Fernie and Letcher, 2010) or on the little owl in Belgium (Jaspers et al., 2005), in which the largest proportion of total OHPs was contributed by PCBs, followed by PBDEs and/or DDTs. This may be attributed to the relatively small contribution of China to the global production and consumption on PCBs (Xing et al., 2005), along with the historically agrochemical influence in the studied region.

Risk assessments were conducted only for PCBs, PBDEs, and DDTs because of the lack of toxicological data on HBCDs and DP. Hazard quotients (HQs) were determined to provide a preliminary risk assessment to birds of prey. HQs are calculated by dividing the measured concentration (MEC) of contaminants in the studied predators with toxicity reference values (TRVs) identified for those chemicals (Lam et al., 2005). In this study, the MECs were replaced by median contaminant concentrations in each species, and the TRVs were derived from no-observed-effect-level (NOEL) or lowest-observed-effect-level (LOEL) concentrations in previously toxicological studies. For interpretation, an HQ <0.1 indicates no hazard, 0.1–1 a low hazard, 1–10 a moderate hazard, and >10 a high hazard (Lemly, 1996).

The total toxic equivalent concentrations ( $\Sigma$ TEQ) were calculated by summing TEQs of major coplanar PCB congeners (i.e., CB-105, -118, -156, and -167). The avian toxic equivalency factors (TEFs) proposed by the World Health Organization (WHO) (Van den Berg et al., 1998) was used to calculate TEQs. The HQs of  $\Sigma$ TEQ<sub>WHO-Avian</sub> in the kestrels and owls were 0.020 and 0.041  $\mu\text{g g}^{-1}$  ww, respectively, by applying an LOEL of 210  $\mu\text{g g}^{-1}$  ww for CYP1A induction in bald eagle chicks (Elliott et al., 1996). An NOEL of 4  $\mu\text{g g}^{-1}$  ww for  $\Sigma$ PCBs in bald eagle (*Falconiformes* specie) was reported by Wiemeyer et al. (1993), associated with productivity and shell thickness. McLane and Hughes (1980) suggested an NOEL of 7  $\mu\text{g g}^{-1}$  ww for screech owls exposed to Aroclor 1248 via diet. The HQs of  $\Sigma$ PCBs were 0.042 and 0.038 for kestrels

and owls, estimated by the corresponding TRV above. These results suggested that PCBs may cause no hazard to the studied predatory species. The HQs of PBDEs in kestrels and owls were calculated based on the reported LOEL, associated with impaired pipping and hatching success in American kestrels, of 1800  $\text{ng g}^{-1}$  wet wt (McKernan et al., 2009). HQs of PBDEs were 0.067 for kestrels and 0.095 for owls, also suggesting no hazard to the reproductive performance of both species in the studied region. An NOEL of 3  $\mu\text{g g}^{-1}$  ww for *p,p'*-DDE, associated with reproduction success, was suggested to peregrine falcon and other *falconiformes* species (Fyfe et al., 1976). For owls, an LOEL of 12  $\mu\text{g g}^{-1}$  ww was selected as TRV to estimate the HQ, where eggshell thinning and reproductive toxicity were observed for barn owls (Mendenhall et al., 1983). According to these TRVs, the HQs of *p,p'*-DDE for kestrels and owls were 0.15 and 0.32, indicating DDTs may pose a low hazard to both species. Additionally, the mixture effects among different chemicals can also be responsible for detrimental health effects. For example, it has been shown that PBDEs can interact with PCBs to cause developmental neurotoxic effects in mice when exposed during a critical period of neonatal brain development (Eriksson et al., 2006). Thus, the risk assessments above might underestimate the actual risk.

### 3.2. Compound-specific accumulation characteristics of OHPs

#### 3.2.1. DDTs and PCBs

Among the DDTs analyzed, *p,p'*-DDE was detectable in all samples and constituted more than 97% of  $\Sigma$ DDTs, which was consistent with the most previous publications (Fernie and Letcher, 2010; Jaspers et al., 2005, 2006). For PCBs, CB-153, -138, -180, and -118 were the most abundant congeners in all the species (Fig. 1). This congener profile is also the common pattern for birds of prey (Jaspers et al., 2006). From the sparrows to the kestrels, the relative abundances of low chlorinated homologues (tri- to tetra-) decreased, whereas those of medium chlorinated homologues (penta- to hepta-) increased. On the contrary, from the rats to the owls, the abundances of low chlorinated homologues (tri- to penta-) increased but those of medium chlorinated homologues (hex- and hepta-) decreased (Fig. 1). The difference in the change of homologue profile between the two prey–predator relationships could be associated with the inter-species differences in

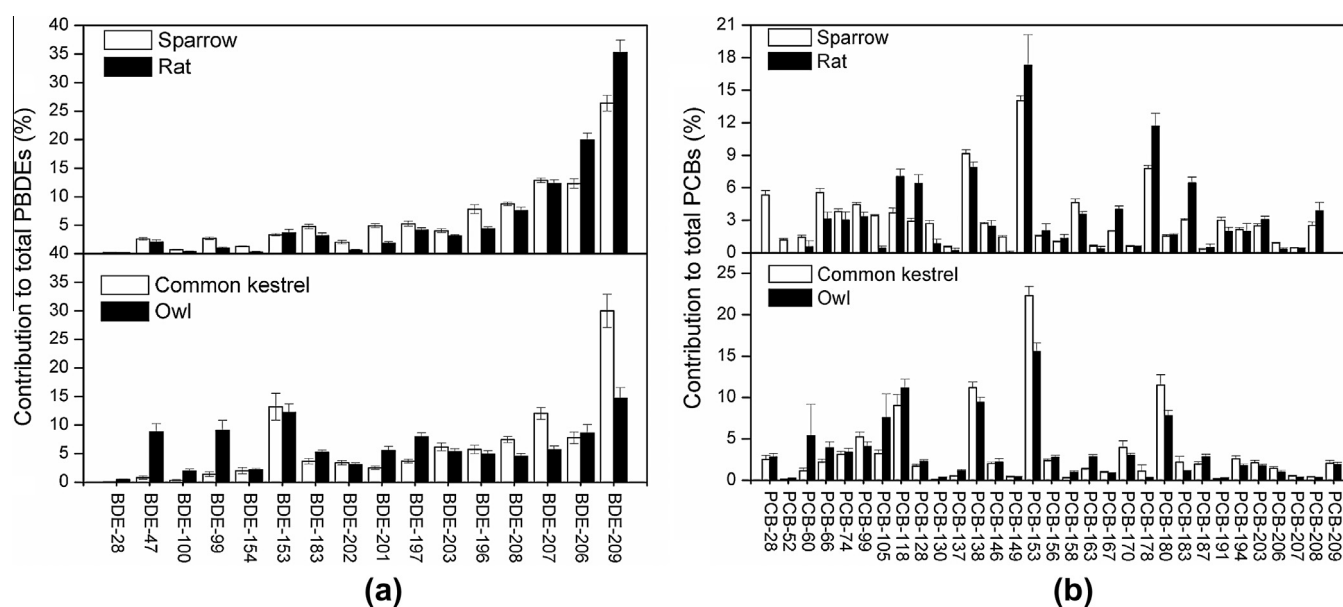


Fig. 1. Congener profiles of (a) PBDEs and (b) PCBs in the sampled species.

metabolic capacity as well as the elimination capacity for PCB congeners. The dechlorination of highly chlorinated congeners occurred in predators would result in a homologue profile shift with more low chlorinated homologues whereas the oxidation of PCBs in predators would result in a more abundance of higher chlorinated homologues since low chlorinated homologues are readily metabolized.

### 3.2.2. PBDEs

Distinct PBDE congener patterns were observed between the common kestrels and owls, with relatively large contributions of lower brominated congeners in the owls while high contributions of highly brominated congeners in the common kestrels (Fig. 1). Given that sparrows and rats share similar PBDE congener patterns, the difference in PBDE congener pattern between the two predatory species cannot be explained by prey diet discrimination. Species-specific biotransformation capacity may be one cause of such pattern shift. BDE-202 is not present in technical mixtures and it has been identified as a debrominated congener of BDE-209 in biota (La Guardia et al., 2007; Stapleton et al., 2004). Thus, the ratio of BDE-202 to BDE-209 was calculated to evaluate the biotransformation potential for highly brominated congeners in the two predatory species. The ratios of BDE-202/BDE-209 in the common kestrels were in the same range as those of the sparrows (Fig. 2). By contrast, the ratio of BDE-202/BDE-209 in the owls exhibited a sharp increase compared with that in the rats (mean of 0.02 in rats to mean of 0.30 in owls). This result clearly demonstrated a possible greater *in vivo* biotransformation of highly brominated BDE congeners in owls than in kestrels. Apart from prey diet, predatory bird can also obtain PBDEs from other routes, such as preening behavior. Therefore, the high percentage of lower brominated congeners in owls can also arise from other PBDE sources existing in urban environment.

### 3.2.3. HBCDs

$\alpha$ -HBCD was the dominant diastereoisomer, accounting for 73% (mean), 96%, 91%, and 96% of total HBCDs in the common kestrels, owls, sparrows, and rats, respectively, which was in line with most reports on HBCD diastereoisomeric patterns in biota (Covaci et al., 2006). The EF of  $\alpha$ -HBCD in all the species were significantly lower ( $t$  test,  $p < 0.05$ ) than the value of the standard solution (mean  $\pm$  SD =  $0.506 \pm 0.007$ ), suggesting an enrichment of ( $-$ )- $\alpha$ -HBCD in the studied species (Table 1). Nevertheless, this conclusion should be interpreted cautiously. For example, the EF $_{\alpha}$  in the common kestrels was 0.25. The common kestrels were therefore expected to accumulate relatively more ( $-$ )- $\alpha$ -HBCD. When compared with its main prey (sparrow), however, the common kestrels

showed a higher EF value (0.25 vs. 0.12), suggesting that common kestrels metabolize ( $-$ )- $\alpha$ -HBCD more readily than ( $+$ )- $\alpha$ -HBCD—a conclusion contrary to the expectation.

A higher fraction of ( $-$ )- $\alpha$ -HBCD was also reported for peregrine falcons from Sweden (Janák et al., 2008) and Canada (Guerra et al., 2012). Selective uptake and/or degradation of either the enantiomer may result in the enrichment of ( $-$ )- $\alpha$ -HBCD (Guerra et al., 2012). An *in vitro* experiment using rat liver microsomes revealed a longer half-life for ( $-$ )- $\alpha$ -HBCD than ( $+$ )- $\alpha$ -HBCD, supporting the aforementioned hypothesis (Esslinger et al., 2011). Conversely, enrichment of ( $+$ )- $\alpha$ -HBCD was observed in white-tailed sea eagle and guillemot from Scandinavia (Janák et al., 2008) and Chinese pond heron from South China (He et al., 2010). These results suggest that EF values of  $\alpha$ -HBCD might be species dependent.

A few studies have focused on the transfer of HBCD enantiomers along food chains. Tomy et al. (2008a) found a strong positive relationship between the fraction of ( $-$ )- $\alpha$ -HBCD and trophic level, indicating the greater bioaccumulation potential of the ( $-$ )- $\alpha$ -enantiomer and/or the greater metabolic susceptibility of the ( $+$ )  $\alpha$ -enantiomer along with increasing trophic level. However, Janák et al. (2008) observed a shift from the relative accumulation of ( $-$ )- $\alpha$ -HBCD in prey (herring, 0.24) to the relative accumulation of ( $+$ )- $\alpha$ -HBCD in predators (guillemot, 0.53). This result accorded with our observations from the sparrows (0.12) to the kestrels (0.25).

### 3.2.4. DP

The fractions of *anti*-DP ( $f_{anti}$ ), defined as the concentration of *anti*-DP divided by total DP, were  $0.79 \pm 0.06$ ,  $0.79 \pm 0.12$ ,  $0.75 \pm 0.06$ , and  $0.77 \pm 0.11$  in the common kestrels, owls, sparrows, and rats, respectively, showing no inter-species differences (one-way ANOVA,  $p > 0.05$ , Table 1). The values of  $f_{anti}$  were close to the measured value ( $f_{anti} = 0.77 \pm 0.02$ ) in three commercial DP products purchased from the domestic chemical market ( $t$ -test,  $p > 0.05$ ), suggesting similar bioaccumulation factors for both DP isomers. This seems contrast with the situation in aquatic biota. *Syn*-DP exhibited a higher assimilation efficiency and a lower depuration rate than did *anti*-DP in a feeding study on juvenile rainbow trout (Tomy et al., 2008b). However, this case may not hold true for terrestrial ecosystems. The  $f_{anti}$  in most terrestrial biota samples fell in the same range as that of commercial DP products or were similar to that in surrounding environments (Xian et al., 2011). A study on Sprague–Dawley rats (Li et al., 2012) exposed to technical DP demonstrated a complex stereoselectivity on DP bioaccumulation in biota. In the low DP level exposure group, no stereoselectivity was found. In the high DP level exposure group, however, an obvious preference for *syn*-DP was observed. Therefore, it may be assumed that stereoselectivity in the bioaccumulation of DP was influenced by highly complex factors and requires further study.

An authentic mono-dechlorination product of *anti*-DP, termed as *anti*-Cl<sub>11</sub>-DP (IUPAC name: 1,6,7,8,9,14,15,16,17,17,18-octa-deca-7,15-diene), was detected in approximately 30% of the samples. A strong positive correlation (Pearson's correlation,  $r^2 = 0.68$ ,  $p < 0.01$ ) between *anti*-Cl<sub>11</sub>-DP and *anti*-DP was revealed in all the detectable samples (Fig. S2), suggesting that *anti*-Cl<sub>11</sub>-DP was biotransformed from *anti*-DP and/or accumulated along with *anti*-DP from the environmental matrix. Zheng et al. (2010) suggested that *anti*-Cl<sub>11</sub>-DP in human hair was likely to accumulate from environmental matrix rather than from *in vivo* biotransformation. However, using serum as monitor tissue, Yan et al. (2012) implied that at least part of the *anti*-Cl<sub>11</sub>-DP in human serum was derived from the *in vivo* metabolism of DP. This result was supported by a previous study conducted by Zhang et al. (2011), in which a possible hepatic dechlorination of *anti*-DP in northern snakehead was found according to its significantly greater ratio

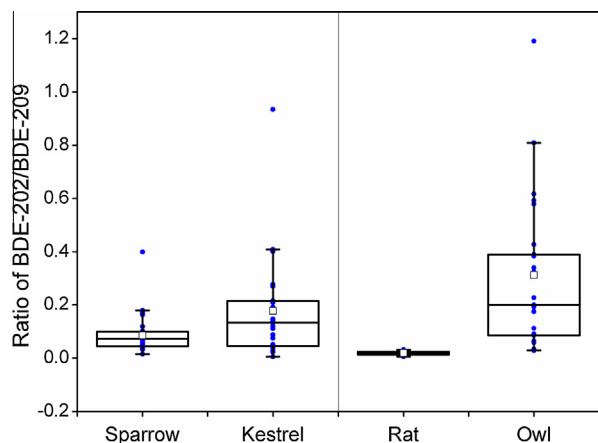


Fig. 2. Ratios of BDE-202/BDE-209 in the investigated samples.

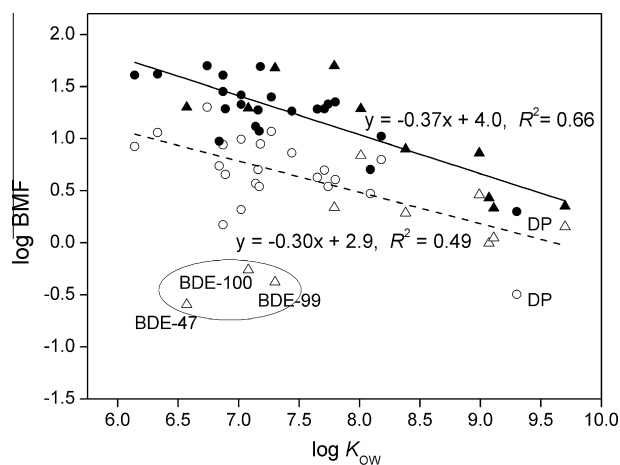


of *anti*-Cl<sub>11</sub>-DP to *anti*-DP in liver than in muscle. In the current study, the average ratios of *anti*-Cl<sub>11</sub>-DP to *anti*-DP (mean ± SD) were 0.038 ± 0.024, 0.048 ± 0.035, and 0.011 ± 0.012 for the kestrels, owls and sparrows, respectively. The kestrels have a higher ratio than do the sparrows, which may suggest an expectedly greater metabolic capacity on *anti*-DP in predators than in prey.

### 3.3. Biomagnification in two predatory food chains

Biomagnification of OHPs within terrestrial avian food chains has rarely been studied, especially for DP and HBCDs. Using median concentrations, we examined the BMF values (the lipid-normalized concentrations of predators divided by that of prey) of the investigated OHPs in the two predatory food chains (Table A.1). Since the sparrow is the primary food item of the common kestrel, and the brown rat, as a typical rodent in the studied area, accounts for the majority of the owl's diet, BMFs calculated from the sparrow–kestrel and rat–owl feeding relationships were adopted.

The calculated BMFs of all the studied compounds were larger than 1 in the rat–owl food chain, indicating biomagnification in this food chain. Regarding the sparrow–kestrel food chain, the BMF values were generally lower than those in the rat–owl food chain for all the compounds. Additionally,  $\alpha$ -HBCD, DP, and several BDE congeners exhibited biodilution. This result suggested that owls have greater potential to accumulate pollutants via food chains than do common kestrels. The relationships between log BMF and log  $K_{OW}$  revealed that all the PCB and PBDE congeners follow a similar function in the two investigated food chains, which is log BMF decreased with increasing log  $K_{OW}$ , except for BDE-47, -99, and -100 in the sparrow–kestrel food chain (Fig. 3). A parabolic relationship between bioaccumulation factors, such as biota-sediment accumulation factor, trophic magnification factors, and log  $K_{OW}$ , was commonly found in many studies on bioaccumulation of OHPs (de Bruyn et al., 2009; Wu et al., 2009). The bioaccumulation factors were maximized for compounds with a log  $K_{OW}$  of approximately 6–7. In the present study, the decline trend with increasing log  $K_{OW}$  could be attributed to the high log  $K_{OW}$  of the concerned compounds with log  $K_{OW}$  ranging from 6.0 to 10 (Fig. 3). The lower BMF values of BDE-47, -99, and -100 in the sparrow–kestrel chain may be due to the rapid elimination rate of these compounds in kestrel species. In a laboratory study, in which American kestrels were exposed to Penta-BDE mixture, these three congeners showed a more rapid elimination rate than BDE-153 (Drouillard et al., 2007).



**Fig. 3.** Relationship between the BMFs and log  $K_{OW}$  of PBDEs (triangles) and PCBs (circles) in the sparrow–kestrel and rat–owl food chains. Log  $K_{OW}$  values were taken from de Bruyn et al. (2009).

To our knowledge, little data was available on the biomagnification of HBCDs in terrestrial system. The only relevant BMF values (range of 2.8–75 and 7.1–51 for  $\alpha$ - and  $\gamma$ -HBCD, respectively) were calculated by He et al. (2010) from grain to spotted dove (the terrestrial phytophagous bird), suggesting biomagnification. In the present study, the BMF of  $\alpha$ -HBCD was >1 in the rat–owl food chain, which was in line with previous studies. However, the BMF of  $\alpha$ -HBCD in the sparrow–kestrel food chain was less than 1 (Table A.1), which contradicted most aquatic studies wherein biomagnification potential was observed for  $\alpha$ -HBCD (Covaci et al., 2006; Tomy et al., 2008a). Similarities were also found for DP in the studied food chains. The BMF values of  $\Sigma$ DP were 2.0 in the rat–owl feeding relationship whereas 0.32 in the sparrow–kestrel food chain (Table A.1). No significant differences were found for the BMF values of two DP isomers in the two feeding relationships (Table A.1). This result again agreed with the  $f_{anti}$  discussion above, and supported the hypothesis that stereoselective accumulation rarely occurred in the studied birds.

## 4. Conclusions

This study showed the occurrence of legacy and emerging OHPs in two terrestrial predatory food chains in a metropolis in North China, with the predominant pollutants being DDTs, followed by PBDEs, PCBs, HBCDs, and DP. PBDEs exhibited a diverse profile in the two predators, with relatively high contributions of lower brominated congeners in the owls than in the common kestrels. Species-dependent biotransformation capacity may be attributed to such a pattern shift.  $\alpha$ -HBCD was the predominant diastereoisomer with preferential enrichment of the (–)-enantiomer in all the detectable samples. No stereoselective bioaccumulation was observed for DP. All the chemicals studied exhibited biomagnification, with BMFs larger than 1 in the rat–owl food chain. However this is not the case for the sparrow–kestrel food chain, indicating the food chain-specific biomagnification potential of OHPs. Except for BDE-47, -99, and -100 in the sparrow–kestrel food chain, the relationships between log BMF and log  $K_{OW}$  of PCBs and PBDEs follow a similar function in the two food chains.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.06.023>.

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