Ecotoxicology and Environmental Safety 223 (2021) 112541

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

# Occurrence and risks of PCDD/Fs and PCBs in three raptors from North China

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ARTICLE INFO

Edited by Dr. Caterina Faggio

*Keywords:*
PCDD/Fs
PCBs
Raptor
TEQ

ABSTRACT

Concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) were investigated in muscle samples from common kestrels (*Falco tinnunculus*), eagle owls (*Bubo bubo),* and little owls (*Athene noctua*) collected in Beijing, China. The concentrations of PCDD/Fs were in the ranges of 22.7–5280, 67.5–1610, and 68.4–3180 pg/g lipid weight (lw), while levels of dioxin-like PCBs ranged from 4.91 to 1560, 8.08–294, and 28.2–3540 ng/g lw, in common kestrel, eagle owl, and little owl, respectively. The main PCDD/Fs congener was 2,3,4,7,8-PeCDF, and CB-153 dominated the seven indicator PCBs. PCB levels have shown a decreasing trend in the last decade for the common kestrel, but not for little owl in Beijing, which exhibited higher levels of pollutants and toxic equivalency (TEQ) values than the other two species. Concentrations of PCDD/Fs, dioxin-like PCBs, and indicator PCBs differed between fledgling and adult raptors for certain species. Raptors in this study generally had a higher TEQ than the no-observed-effect level in the literature, indicating significant exposure risks to PCDD/Fs and dioxin-like PCBs in raptors, especially in adult little owls.

## 1. Introduction

Human activities have a significant impact on biological diversity worldwide. In many hotspots of biological diversity, the habitats of wild animals are disappearing or degenerating rapidly due to the increasing densities of cities and the development of agricultural activities (Benedikter and Siepmann, 2015). The destruction of habitats remarkably influences wildlife populations, and chemical contamination is a crucial factor that indirectly threatens biological diversity. For example, persistent organic pollutants (POPs), such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), are toxic to wildlife (Cizdziel et al., 2013).

POPs are characterized by their persistence, bioaccumulation, semi-volatility, and mobility of long-range transport. The hydrophobic nature and resistance of most POPs to metabolism in organisms leads to their high bioaccumulation potential (Abalos et al., 2008). POPs are transferred via the food chain, become concentrated in the tissues of organisms at high trophic levels in food chains, and generate toxic effects (Elliott et al., 2015). Due to the widespread and diverse feed items of birds in the environment, they have been frequently used as bio-indicators of environmental contamination (Chen et al., 2010a, 2010b). Raptors are particularly sensitive to environmental pollution because of their apex position in the food chain (Chen et al., 2009; Yu et al., 2011). Several long-term monitoring studies have been conducted on raptors to trace the occurrence and temporal trend of POPs in the environment (Jaspers et al., 2008; Bustnes et al., 2011; Garcia-Fernandez et al., 2013).

Although many studies have reported the occurrence of POPs in raptors, the highly variable concentrations and profiles of POPs in literature restrict our ability to understand the bioaccumulation process and potential adverse effects of POPs in raptors (Chen et al., 2010a, 2010b). Eggs of European sparrowhawk (*Accipiter nisus*), common buzzard (*Buteo buteo*), and grey heron (*Ardea cinerea*) showed significant differences in the concentrations and compositions of POPs, which was

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https://doi.org/10.1016/j.ecoenv.2021.112541
Received 2 June 2021; Received in revised form 16 July 2021; Accepted 19 July 2021
Available online 2 August 2021
0147-6513/

due to the different foraging sites and feeding habits of the three bird species (Wiesmüller et al., 2002). Some studies have already revealed that variable concentrations of POPs in birds are associated with age, gender, and sampling region (Bustnes et al., 2011; Jaspers et al., 2006; Kubota et al., 2013). For example, PCDD levels in liver samples of white-breasted cormorants (*Phalacrocorax lucidus*) from Lake Biwa in Japan showed gender differences (Kubota et al., 2013). The male-to-female concentration ratios for PCDD congeners significantly decreased with the liver-to-muscle concentration ratios of PCDDs (Kubota et al., 2013). In contrast, a negative correlation was observed between the above ratios of PCDFs (Kubota et al., 2013). Eggs are frequently used in studies of POPs in avian species, followed by nestlings and adult birds (Abbasi et al., 2016). Nestlings were considered to represent the pollution residue in eggs and recent pollution near the bird's habitat (Coefield et al., 2010; Eulaers et al., 2011). However, the long-term bioaccumulation of POPs during different growth stages of birds has rarely been discussed in the literature, partly because of the difficulties in tracing contaminants in wild bird nestlings, fledglings, and adults (Elliot et al., 2001). Therefore, it remains a challenge to evaluate the pollution status and toxic effects of POPs on birds at different growth stages.

PCDD/Fs and dioxin-like PCBs (DL-PCBs) are among the most toxic POPs and can have diverse adverse effects, including reproductive impairments, developmental deformities, immune deficiency, and cardiovascular dysfunction in avian species (Domingo and Bocio, 2007). Thus, it is important to know the residue levels and potential risks of PCDDs and DL-PCBs in wildlife, especially those at high trophic levels, such as raptors. However, very few studies have reported contamination of PCDD/Fs and DL-PCBs in birds from China (Wang et al., 2012). The bioaccumulation of PCDD/Fs and PCBs in different species, genders, and ages of raptors is still unclear. Previously, we revealed the distribution of polybrominated diphenyl ethers (PBDEs) in feathers and muscles of raptors from Beijing, China (Yin et al., 2018). Three terrestrial avian predators, including common kestrel (*Falco tinnunculus*), eagle owl (*Bubo bubo*), and little owl (*Athene noctua*), were collected. The present study focuses on the pollution and toxicological risks of PCDD/Fs and PCBs in raptors from Beijing. In addition, the study also aimed to explore the influence of species, gender, and age on the concentrations and composition profiles of PCDD/Fs and PCBs. The results will provide essential information on the contamination and risks of dioxin-like chemicals in raptors and will contribute to our understanding of the bioaccumulation features and toxicological risks of POPs to the study species.

## 2. Methods

### *2.1. Sample collection*

The common kestrel (CK, n = 25), eagle owl (EO, n = 10), and little owl (LO, n = 7) samples were collected from 2014 to 2016 by the Beijing Raptor Rescue Center (BRRC) in Beijing, China. The specimens were either dead, died during attempted rehabilitation, or were euthanized at BRRC due to serious injuries. The muscle samples were wrapped in aluminum foil and kept in a freezer at − 20 °C until dissection in preparation for analysis. Gender and age information were also recorded during the dissection of the birds.

### *2.2. Sample extraction and treatment*

The analysis of PCDD/Fs and PCBs in this study followed the US EPA methods (1613B, 1668A). The muscle samples were freeze-dried and then weighed using an electronic balance. Approximately 2 g of muscle was accurately weighed, before 10 g of anhydrous sodium sulfate ($Na_2SO_4$) was added for vigorous mixing and grinding. The samples were then extracted via accelerated solvent extraction (ASE, ASE300, Dionex, USA). $^{13}$C-labeled internal standards (1613-LCS, 68A-LCS) were spiked into the samples before extraction. The extracts were cleaned using a multilayer silica gel column, followed by an activated carbon column. The eluant was concentrated to approximately 25 μL for instrumental analysis. $^{13}$C-labeled recovery standards (1613-IS, 68A-IS) were added to the solutions prior to instrumental analysis. Lipid content was measured by the gravimetric method, and moisture content was calculated through weight measurements before and after freeze-drying. All data presented here are expressed as lipid weight (lw), except when compared with published data on wet weight (ww).

### *2.3. Instrument analysis*

PCDD/Fs and PCBs were quantified via high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS) systems, AutoSpec Ultima (Waters Micromass, UK), using an electron impact ($EI^+$) ion source. The solution (1 μL) was injected into the HRGC in splitless mode with a 60 m DB-5MS fused silica capillary column (J&W Scientific, 0.25 μm film thickness, 0.25 mm i.d.). In total, 17 2,3,7,8-substituted PCDD/Fs, 12 DL-PCBs (CBs-77, -81, -105, -114, -118, -123, -126, -156, -157, -167, -169, and -189), and six indicator PCBs (CBs-28, -52, -101, -138, -153, and -180) were quantified. Instrument details can be found in a previous study (Zheng et al., 2018). The target contaminants are presented in Table S1.

### *2.4. QA/QC*

The analysis of PCDD/Fs and PCBs in this study followed the US EPA methods (1613 B, 1668A). The limit of detection (LOD) was set as the response at three signal/noise ratios for the target compounds. The LOD values for PCDD/Fs and PCBs were in the ranges 0.05–4.76 pg/g lw and 0.12–40.7 pg/g lw, respectively. Quality control included the analysis of blanks, recoveries of surrogate standards, and recoveries of spiked standards. Samples spiked with target PCBs and PCDD/Fs were analyzed in triplicate. $^{13}$C-labeled internal standards (1613-LCS, 68A-LCS) and surrogate standards (1613-IS, 68A-IS) were added for quantification and quality control. The recovery rates for PCBs and PCDD/Fs were 43.6-149% and 52.4–87%, respectively. The relative standard deviation was < 15%. Laboratory blank samples were routinely quantified, and in most cases, the blank values were below the LOD values, with the exception being lower than 15% of the targets in the samples. Therefore, the reported results were not corrected with blanks.

### *2.5. Statistical analysis*

All statistical analyses were performed using SPSS 22.0 software. The concentrations below the LOD were set to half of the LOD before statistical analysis. Concentrations of individual congeners were not normally distributed before and after log-transformation. The Mann-Whitney test was used to test the significance of differences between different groups of samples. Spearman rank analysis was used to test the correlations between levels of the different pollutants. Significance was set at $p < 0.05$ and $p < 0.01$.

## 3. Results and discussion

### *3.1. Pollutant concentrations*

The detection frequencies and pollutant concentrations are summarized in Tables 1 and 2 for PCDD/Fs and PCBs, respectively. DL-PCBs and indicator PCBs were detected in most samples, while some PCDD/Fs such as 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF, and 1,2,3,7,8,9-HxCDD were found in less than 50% of samples for the three bird species. For common kestrels, concentrations of PCDD/Fs, DL- PCBs, and indicator PCBs were in the ranges 22.7–5280 pg/g lw (median: 357 pg/g lw), 4.91–1560 ng/g lw (median: 48.1 ng/g lw), and 33.1–7950 ng/g lw (median: 382 ng/g lw), respectively. In eagle owls, the concentration

**Table 1**
DFs and concentrations of PCDD/Fs (pg/g lw) in muscle samples.

| | Common Kestrel | | Eagle Owl | | Little Owl | |
|---|---|---|---|---|---|---|
| | DF | levels | DF | levels | DF | levels |
| Lipid% | | 14.5 ± 5.7 | | 13.2 ± 4.4 | | 10.4 ± 4.7 |
| 2,3,7,8-TCDF | 96% | 31.5 (nd-1690) | 100% | 20.4 (7.11–201) | 57% | 4.29 (nd-38.0) |
| 1,2,3,7,8-PeCDF | 96% | 23.3 (nd-892) | 100% | 15.4 (3.37–124) | 43% | nd-67.0 |
| 2,3,4,7,8-PeCDF | 100% | 108 (7.06–1440) | 100% | 41.6 (12.6–298) | 100% | 185 (19.1–1360) |
| 1,2,3,4,7,8-HxCDF | 100% | 32.0 (2.52–334) | 100% | 18.8 (10.5–138) | 86% | 16.4 (nd-159) |
| 1,2,3,6,7,8-HxCDF | 100% | 26.6 (1.96–216) | 100% | 20.2 (7.78–227) | 71% | 11.7 (nd-79.7) |
| 2,3,4,6,7,8-HxCDF | 88% | 12.7 (nd-93.2) | 80% | 8.01 (nd-90.1) | 57% | 2.57 (nd-30.2) |
| 1,2,3,7,8,9-HxCDF | 36% | nd-7.41 | 20% | nd-10.6 | 43% | nd-15.8 |
| 1,2,3,4,6,7,8-HpCDF | 96% | 8.33 (nd-288) | 80% | 12.2 (nd-366) | 71% | 2.06 (nd-7.85) |
| 1,2,3,4,7,8,9-HpCDF | 48% | nd-70.7 | 40% | nd-11.8 | 29% | nd-12.1 |
| OCDF | 58% | 6.89 (nd-301) | 50% | 1.98 (nd-168) | 57% | 0.73 (nd-9.18) |
| 2,3,7,8-TCDD | 84% | 7.30 (nd-217) | 80% | 4.11 (nd-46.2) | 43% | nd-262 |
| 1,2,3,7,8-PeCDD | 96% | 26.0 (nd-477) | 80% | 11.2 (nd-90.9) | 71% | 35.2 (nd-954) |
| 1,2,3,4,7,8-HxCDD | 88% | 7.23 (nd-92.3) | 60% | 2.56 (nd-42.8) | 43% | nd-80.8 |
| 1,2,3,6,7,8-HxCDD | 100% | 20.5 (0.62–278) | 90% | 11.0 (nd-139) | 86% | 9.25 (nd-253) |
| 1,2,3,7,8,9-HxCDD | 56% | 1.31 (nd-9.48) | 20% | nd-21.3 | 29% | nd-3.62 |
| 1,2,3,4,6,7,8-HpCDD | 92% | 5.10 (nd-1790) | 90% | 6.97 (nd-88.6) | 71% | 1.72 (nd-5.47) |
| OCDD | 96% | 11.9 (nd-2120) | 60% | 6.06 (nd-171) | 86% | 18.1 (nd-775) |
| ∑PCDD/Fs | 100% | 357 (22.7–5280) | 100% | 232 (67.5–1610) | 100% | 392 (68.4–3180) |

**Table 2**
DFs and concentrations of PCBs (ng/g lw) in muscle samples.

| | Common Kestrel | | Eagle Owl | | Little Owl | |
|---|---|---|---|---|---|---|
| | DF | levels | DF | levels | DF | levels |
| Lipid% | | 14.5 ± 5.7 | | 13.2 ± 4.4 | | 10.4 ± 4.7 |
| Dioxin-like PCBs | | | | | | |
| CB 77 | 100% | 0.32 (0.05–10.6) | 100% | 0.08 (0.02–0.87) | 86% | 0.03 (nd-0.29) |
| CB 81 | 100% | 0.18 (nd-3.39) | 100% | 0.08 (0.03–1.03) | 100% | 0.26 (0.07–1.76) |
| CB 105 | 100% | 4.50 (0.23–216) | 100% | 3.99 (1.37–37.4) | 100% | 19.8 (3.28–246) |
| CB 114 | 100% | 1.24 (0.14–42.0) | 100% | 0.77 (0.24–8.20) | 100% | 4.22 (1.18–101) |
| CB 118 | 100% | 18.4 (1.30–864) | 100% | 16.2 (4.42–142) | 100% | 81.1 (9.83–1020) |
| CB 123 | 100% | 0.38 (0.03–23.3) | 100% | 0.28 (0.06–3.33) | 100% | 2.06 (0.47–47.9) |
| CB 126 | 100% | 0.61 (0.06–14.6) | 100% | 0.27 (0.06–1.93) | 100% | 0.79 (0.28–9.35) |
| CB 156 | 100% | 6.62 (1.06–189) | 100% | 4.65 (0.77–61.0) | 100% | 39.6 (4.10–962) |
| CB 157 | 100% | 1.72 (0.15–34.7) | 100% | 1.00 (0.22–11.8) | 100% | 10.4 (1.45–226) |
| CB 167 | 100% | 2.98 (0.53–88.8) | 100% | 1.55 (0.25–23.2) | 100% | 14.2 (2.19–346) |
| CB 169 | 100% | 0.45 (0.07–13.2) | 100% | 0.23 (0.07–3.40) | 100% | 2.48 (0.54–52.2) |
| CB 189 | 100% | 2.65 (0.32–59.0) | 100% | 1.42 (0.24–37.5) | 100% | 12.9 (2.30–519) |
| $\sum_{\text{dioxin-like}}$PCBs | 100% | 48.1 (4.91–1560) | 100% | 31.1 (8.08–294) | 100% | 200 (28.2–3540) |
| Indicator PCBs | | | | | | |
| CB 28 | 100% | 5.10 (0.61–53.0) | 100% | 2.65 (2.07–121) | 100% | 4.74 (3.20–39.4) |
| CB 52 | 96% | 0.11 (nd-11.3) | 100% | 0.15 (0.11–6.52) | 100% | 0.41 (0.15–45.4) |
| CB 101 | 100% | 0.58 (0.11–11.2) | 100% | 1.49 (0.41–16.6) | 100% | 9.37 (0.04–27.4) |
| CB 138 | 100% | 62.0 (5.04–1160) | 100% | 61.0 (6.56–860) | 100% | 309 (22.4–2780) |
| CB 153 | 100% | 186 (11.7–4580) | 100% | 162 (20.9–2650) | 100% | 906 (44.9–9700) |
| CB 180 | 100% | 55.3 (6.05–2470) | 100% | 21.8 (2.30–572) | 100% | 220 (21.9–4720) |
| $\sum_7$PCBs | 100% | 382 (33.1–7950) | 100% | 308 (37.5–4360) | 100% | 1620 (103–18300) |

ranges of those contaminants were 67.5–1610 pg/g lw, 8.08–294 ng/g lw, and 28.2–3540 ng/g lw, respectively. Contaminant levels in little owls were 68.4–3180 pg/g lw, 37.5–4360 ng/g lw, and 103–18,300 ng/g lw, respectively. The levels of indicator PCBs were much higher than those of PCDD/Fs and DL-PCBs in all three raptor species. Concentrations of indicator PCBs were significantly correlated with those of DL-PCBs ($p < 0.01$), suggesting that PCBs are an effective indicator of PCB contamination.

LOs had lower detection frequencies of PCDD/F congeners than CKs and EOs, while all three raptor species had similar median levels of total PCDD/Fs (medians of 357, 232, and 392 pg/g lw for CKs, EOs, and LOs, respectively). The levels of DL-PCBs and indicator PCBs in CKs and EOs were much lower than those in LOs, but the differences were not significant ($p > 0.05$). Only a limited number of studies have reported the occurrence of PCDD/Fs in raptors (Jiménez et al., 2007; Yoshikawa et al., 2021). Combined concentrations of PCDD/Fs and DL-PCBs were reported by Yoshikawa et al. (2021), which hindered comparisons of PCDD/F levels between different studies. Concentrations of PCDDs and PCDFs were 22.2–43.2 and 2.64–14.2 pg/g wet weight (ww) in red kites (*Milvus milvus*) and western ospreys (*Pandion haliaetus*), respectively (Jiménez et al., 2007), lower than in raptors from Beijing.

The concentrations of PCBs in different tissues of white-tailed sea eagles (*Haliaeetus albicilla*) from West Greenland ranged from 490 to 1.5 $\times$ $10^6$ ng/g lw (Jaspers et al., 2013), which was much higher than the results for raptors from Beijing measured during the present study. Common kestrels and owls from Beijing were also collected in 2004–2005 (Chen et al., 2009) and 2005–2007 (Yu et al., 2013). The median concentrations of PCBs were 3300 and 1500 ng/g lw in common kestrels and little owls during 2004–2005, respectively (Chen et al., 2009). In 2005–2007, the median concentrations of PCBs were 370 and 1300 ng/g in common kestrels and the combined owl samples, respectively (Yu et al., 2013). The results showed a decreasing trend for PCB levels in common kestrels in the last decade, while PCB levels in little owls seemed to be consistent. The observed decline in PCB levels was expected because their use has been banned for decades. However, raptor species showed species-specific bioaccumulation of PCBs in this study, which could be attributed to various foraging sites and prey types. Similarly, LOs had higher levels of PBDEs than CKs and EOs (Yin et al., 2018). CKs in this study mainly feed on small birds, which comprised 89.6% of their food, based on observations of prey deliveries in video recordings (Yu et al., 2011). EOs feed on reptiles, amphibians, birds, and sometimes terrestrial invertebrates. LOs prefer mice, coleoptera, and other small animals (Yin et al., 2018). Mice may be an important source of banned industrial additives such as PCBs and PBDEs(Yin et al, 2018). It is also possible that LOs preferentially foraged near landfills, which have been proven to be the main source of PBDEs and other brominated flame retardants for gulls in the United Kingdom (Tongue et al., 2021).

### 3.2. Congener profiles in the birds

The predominant congener in PCDD/Fs was 2,3,4,7,8-PeCDF, accounting for 31%, 21%, and 45% of PCDD/Fs in CKs, EOs, and LOs, respectively (Fig. 1). LOs had lower proportions of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, and 1,2,3,4,6,7,8-HpCDD, as well as higher proportions of 2,3,4,7,8-PeCDF and OCDD, compared with CKs and EOs. EOs had significantly higher proportions of 1,2,3,4,7,8-HpCDF than CKs and LOs. Moreover, 2,3,4,7,8-PeCDF is mainly derived from technical PCB mixtures and is considered an impurity during the application of PCBs in transformers and capacitors (Elliot et al., 1996). In this study, significant correlations were observed between the levels of 2,3,4,7,8-PeCDF and PCB congeners, indicating similar sources of PCDD/Fs and PCBs ($p < 0.05$). Similar results have been reported for PCDD/Fs in different bird species (Jiménez et al., 2007; Kubota et al., 2013; Wang et al., 2012). Jiménez et al. (2007) found that 2,3,4,7,8-PeCDF and OCDD were the main PCDD/F homologs in the eggs of two raptor species, namely, Red Kite and Western Osprey from Spain. In addition, 2,3,4,7,8-PeCDF was also the predominant PCDD/F congener in water birds from Japan (Kubota et al., 2013), Hong Kong, China (Wang et al., 2012), Norway (Eulaers et al., 2011), and the Mediterranean region (Morales et al., 2016).

The congener profiles of indicator PCBs were consistent among the three raptor species. CB-153 was the predominant PCB congener, accounting for 53–59% of the total indicator PCBs, followed by CBs-138 and -180 (Fig. 2). The composition profiles of PCBs were consistent with those of CKs from Belgium (Jaspers et al., 2006) and CKs collected before 2010 in Beijing (Chen et al., 2009; Yu et al., 2013).

### 3.3. Gender- and age-specific patterns of pollutants

Concentrations of PCDD/Fs, DL-PCBs, and indicator PCBs were compared between males and females, as well as fledglings (< 6 months of age) and adults (> 6 months of age). The results are shown in Figs. S1-S3. Differences in contaminant levels were tested for statistical significance for CKs, but not EOs and LOs because of the limited sample sizes of EOs (n = 10) and LOs (n = 7).

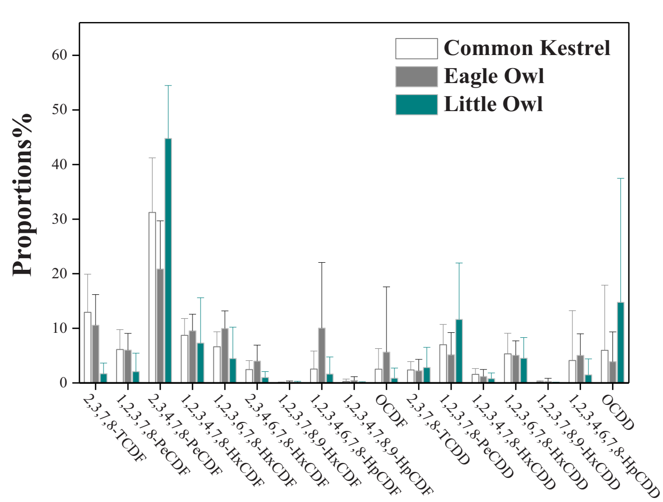


**Fig. 1.** Compositions of PCDD/Fs in muscle samples.

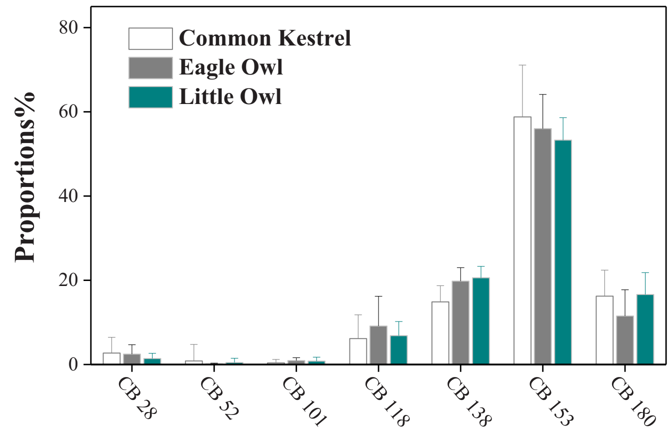


**Fig. 2.** Compositions of indicator PCBs in muscle samples.

Male and female CKs had similar ranges of PCDD/Fs, DL-PCBs, and indicator PCBs, which was also confirmed via statistical analysis ($p > 0.05$). Levels of PCDD/Fs, DL-PCBs, and indicator PCBs were also similar between female and male EOs and LOs. No gender differences were observed for the pollutants in the three raptor species.

Female fledglings and adults of CKs and LOs had similar pollutant ranges. In contrast, male adults generally had higher levels of PCDD/Fs, DL-PCBs, and indicator PCBs than male fledgling CKs and LOs. Different results were observed for EOs. Fledgling EOs had lower concentrations of PCDD/Fs and higher concentrations of PCBs than adult EOs. The results should be interpreted with caution, as only one sample each was available for fledgling female and male EOs. Avian egg pollutants become concentrated in embryos, which results in elevated levels of pollutants in nestlings (Coefield et al., 2010; Eulaers et al., 2011). Young birds may have a lower metabolic capacity for xenobiotic pollutants, which would facilitate the bioaccumulation of pollutants. Additionally, the fast growth of fledglings has a dilution effect on the pollutant levels. The results indicated higher exposure risks of PCDD/Fs and PCBs for adults than fledgling CKs and Eos; however, this finding still requires analysis of more samples for verification.

### 3.4. Risk assessment

Toxic equivalency (TEQ) values were estimated using toxic equivalency factors (TEFs) for PCDD/F congeners and DL-PCB concentrations for birds, according to the probabilistic risk assessment specified by the World Health Organization (Van den Berg et al., 2006) (Fig. 3). TEQs in CKs, EOs, and LOs were 0.03–24.5, 0.18–4.04, and 0.48–29.6 ng/g lw, with medians of 0.76, 0.56, and 2.40 ng/g lw, respectively, or 0.01–1.47, 0.03–0.55, and 0.06–1.28 ng/g ww, with medians of 0.12, 0.07, and 0.20 ng/g ww on a wet weight basis, respectively. TEQs were mainly contributed by 2,3,4,7,8-PeCDF and CB-105. The TEQs of CB-105 were 72%, 75%, and 81%, followed by 2,3,4,7,8-PeCDF, which contributed 12%, 8.7%, and 6.5% of the TEQs of CKs, EOs, and LOs, respectively. CB-114 also contributed significantly to the TEQs, accounting for 6.5%, 4.3%, and 8.8% of the TEQs of CKs, EOs, and LOs, respectively. TEQs were also exhibited separately for raptors of different genders and ages (Fig. 3). A similar range of TEQs was found for males and females of CKs, EOs, and LOs. Adult male CKs and LOs always had higher TEQs than male fledglings, while differences in female fledglings and adults were not consistent among the three raptor species. The results highlighted the significance of dioxin-related toxic effects in adult male CKs and LOs.

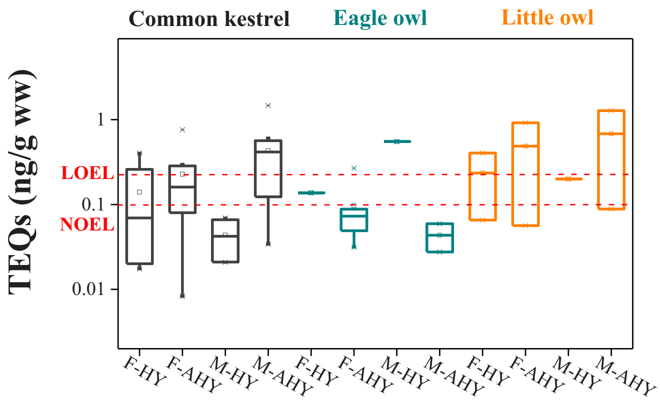


**Fig. 3.** TEQs of bird species. F and M mean female and male, while HY and AHY mean 0–6 month and > 6 month year age. The dotted line represents the NOEL (100 pg/g ww) and LOEL (210 pg/g ww) for bald eagles (Elliot et al., 1996, 2001). Box plots are defined as follows: center line, median; circle symbol, mean; boxplot edges, the 25th and 75th percentiles; whiskers, range of data values.

The results of this study were consistent with the TEQs in a healthy cormorant (*Phalacrocorax carbo*) liver (range: 0.03–0.96 ng/g ww) (Kubota et al., 2013). TEQs of PCDD/Fs in adult and nestling eagle owls in North American region were 9.4 and 2.1 ng ng/kg lw, respectively (Coefield et al., 2010), which were significantly lower than the results of this study. The no-observed-effect level (NOEL) values of TEQs in waterbirds were reported to be 4.6, 7.5, and 10 pg/g ww for cormorant, Caspian tern (*Sterna caspia*), and herring gull (*Larus argentatus*), respectively (Giesy et al., 1994). The NOEL of bald eagle (*Haliaeetus leucocephalus*) was reported to be 100 pg/g ww (Elliot et al., 1996), which was lower than the TEQs in most raptors in this study. The lowest observed effect level (LOEL) values were 20, 130, and 210 pg/g ww for wood ducks (*Aix sponsa*), coast osprey (*Pandion haliaetus*), and bald eagle, respectively (Giesy et al., 1994; Elliot et al., 1996, 2001). In the current study, TEQs up to 1.47 ng/g ww were noted. Approximately 30% of CKs, 20% of EOs, and 50% of LOs in this study had TEQs exceeding the LOEL value for bald eagles. TEQs differed in terms of raptor gender and age. LOs had TEQs generally higher than the NOELs of bald eagles. Adult CKs had higher TEQs than the NOEL, and fledgling EOs had higher TEQs than NOEL. The results indicated that the body burden of PCDD/Fs and PCBs in raptors from Beijing may have resulted in significant toxicological effects, such as reproductive success, egg development, and chick survival. The adverse effects of contaminants on the raptors in Beijing should be considered further.

## 4. Conclusions

PCDD/Fs and PCBs were detected in most individuals of the three raptor species. In raptors, PCDD/Fs and PCBs had similar congener profiles, which were dominated by 2,3,4,7,8-PeCDF and CB-153, respectively. LOs had higher levels of PCDD/Fs, DL-PCBs, and indicator PCBs, as well as higher TEQs, than the other two species, which may be attributed to a more diverse diet and larger foraging areas. Concentrations of PCDD/Fs and PCBs did not show gender differences but differed between fledgling and adult birds. Based on the results of the limited samples, adults seemed to have higher levels of pollutants than fledglings. The studied raptor species had notably high TEQs, and a proportion of samples exceeded published values for NOEL and LOEL. The toxicological effects of dioxins and dioxin-like chemicals on raptors in Beijing warrant more future attention.

## CRediT authorship contribution statement

**Zhengwang Zhang**: Conceptualization, Resources. **Ya Zhang:** Methodology, Data curation, Writing – Original draft preparation. **Xiaobo Zheng:** Visualization, Writing – Reviewing. **Pu Wang:** Software, Validation. **Qinghua Zhang:** Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

This study was financially supported by National Key Research and Development Program of China (No.2017YFC1600301), and the second Wildlife Resources Survey Project of Beijing （No. 230100094）, and the National Natural Science Foundation of China (Nos. 41877361 and 41931290), and Guangdong Foundation for Program of Science and Technology Research (No. 2021A1515011560). We thank the Beijing Raptor Rescue Center (BRRC,China) for collecting the samples.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2021.112541.

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