

Polybrominated Diphenyl Ethers in Birds of Prey from Northern China

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Birds of prey from Northern China (Beijing area) were examined for polybrominated diphenyl ethers (PBDEs). A total of 47 specimens from eight different species were analyzed. Muscle and liver were analyzed separately for each bird. Kidneys were pooled by species. Common kestrels exhibited the highest PBDE levels (mean muscle and liver concentrations of 12 300 and 12 200 ng/g lipid weight, respectively), with maxima in an individual bird of 31 700 in muscle and 40 900 ng/g lw in liver. Congener profiles differed between some species, but were generally dominated by the more brominated congeners (e.g., BDE-153, -209, -183, -207). BDE-209 was especially elevated compared to other published reports. Interspecies differences in congener concentrations and profiles may be due to diet, behavior, or biotransformation capacities. BDE-209 was detected in 79.4% of the samples. Common kestrels contained the highest BDE-209 levels (mean/maxima of 2150/6220 in muscle and 2870/12 200 ng/g lw in liver). BDE-209 was the dominant congener in tissues from some buzzards, scops owls, and long-eared owls. It was the second most abundant congener in common kestrels. The remarkable levels and dominance of BDE-209 may relate to significant production, usage, or disposal of deca-containing products in China. These observations reinforce the growing view that organisms using terrestrial food chains may have greater exposure to BDE-209.

Polybrominated diphenyl ethers (PBDEs) are flame retardant additives widely used in textiles, thermoplastics, polyurethane foams, and electronic products. The three major commercial PBDE mixtures are penta-, octa-, and deca- (1). Previous reports have shown that PBDEs can enter the environment during production, use, disposal, and recycling processes (2–4). Accordingly, some PBDE congeners have become widely distributed in abiotic media, wildlife, and people, reaching even remote areas (5–8). Toxicological studies are limited but suggest that the different congeners possess

varying potencies (9). In some cases observed toxicity may be a function of differential uptake or bioavailability. Effects include impacts on neurodevelopment, thyroid hormone levels, thyroid, liver, and kidney morphology, liver ethoxyresorufin-O-deethylase activity, reproductive success, and fetal toxicity/teratogenicity (9). PBDE levels in the environment have generally been increasing since the 1970s (5, 8). However, some European studies have reported a recent decrease of the less brominated congeners, perhaps as a function of the voluntary cessation of penta- consumption there (8). The European Union banned both penta- and octa- in 2004. The majority of documented global penta use has been in North America. While the major manufacturer there discontinued production in December 2004, recent studies have yet to identify a diminution in wildlife PBDE concentrations (2). Continued usage of deca- has been controversial on both continents, with some concerned about potential health, bioaccumulation, and persistence issues, and others underlining the current lack of scientific documentation of such concerns in real-world scenarios.

In contrast to Europe and North America, few reports have described PBDE burdens in Asia. Particularly lacking are data from China, despite its position as one of the world's largest manufacturers and consumers of textiles, plastics, and electronic products. The 2001 demand for PBDE formulations in Asia consisted primarily of deca- (93.3%), with lesser amounts of octa- (6.1%) and penta- (<1%) (10). It is hence likely that deca- is the predominant formulation in the Chinese market, although survey data are not available. Another issue contributing to PBDE contamination is the transport of obsolete electronic products or "E-wastes" from western countries to China for recycling (11). It has been estimated that 50–70% of U.S. E-wastes generated were exported to China (11). In Guangdong Province, China, for instance, approximately 145 million electronic devices were "recycled" in 2002, containing up to 2.61×10^8 kg of PBDEs (12). Once there, primitive methods are generally used in an attempt to recover valuable metals from the electronics. Large amounts of plastic and electronic parts are either burned or subsequently dumped (11). While a few studies have been performed on Chinese PBDE burdens in sediments (13, 14), air (15, 16), aquatic biota (17, 18), and humans (19), no data are available on terrestrial wildlife. Limited European reports have indicated that terrestrial wildlife may contain elevated proportions of deca- (predominantly BDE-209) (8). In most cases concentrations have been modest and the detection frequencies have been low. An exception has involved predatory birds. For example, a study of Swedish falcons detected BDE-209 in 18 of 21 eggs analyzed at concentrations of up to 430 ng/g lipid weight (20). Other raptor species from Europe (i.e., sparrowhawk, kestrel, buzzard, and owl) have also been reported to contain BDE-209 in tissues or eggs (21, 22). Based on the above considerations we obtained and analyzed PBDE burdens in several raptor species from Northern China.

Materials and Methods

Samples. Birds were obtained from the collection at the Beijing Raptor Rescue Center (BRRRC, China) between March 2004 and January 2006. Species examined were the common kestrel (*Falco tinnunculus*, $N = 6$); sparrowhawk (*Accipiter nisus*, $N = 11$), and Japanese sparrowhawk (*Accipiter gularis*, $N = 6$); scops (*Otus sunia*, $N = 6$), long-eared (*Asio otus*, $N = 6$) and little owl (*Athene noctua*, $N = 6$); and common (*Buteo buteo*, $N = 3$) and upland buzzard (*Buteo hemilasius*, $N = 3$). These species are all listed in China as National Key

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Protected Wild Animals. Accordingly only birds that were received dead, died during attempted rehabilitation, or were euthanized at the Center due to serious injuries were available for sampling. Specimens were maintained intact at $-20\text{ }^{\circ}\text{C}$ until dissected, minimizing potential introduction of contaminants, and were in good condition (showing no signs of decay). See Supporting Information (Table SI-1) for more detailed information (diet and migratory habits) on each species.

Chemicals. All organic solvents used were of pesticide residue analysis grade, and were purchased from Scharlau Chemie (Barcelona, Spain) and Tedia (Fairfield, OH). All native PBDE standards were purchased from AccuStandards, Inc. (New Haven, CT). $^{13}\text{C}_{12}$ -labeled PCB-141 and -208 were obtained from Cambridge Isotope Laboratories (Andover, MA). Unlabeled PCB-204 was purchased from Ultra Scientific (North Kingstown, RI).

Analysis. Pectoral muscle and liver from each bird were excised, weighed, and transferred to residue-grade solvent-rinsed glass jars. These were frozen until initiation of chemical analysis. Due to their small size kidneys were pooled by species. Tissues and sodium sulfate blanks were freeze-dried and then subjected to enhanced solvent extraction (Dionex ASE 300, Sunnyvale, CA), employing two 5-min extraction cycles with dichloromethane (DCM) at $100\text{ }^{\circ}\text{C}$ and 1500 psi, followed by a 60% vessel flush (a solvent flush equivalent to 60% of cell volume is passed through the cell). Before extraction, samples and blanks were spiked with surrogates (PCB-204 and $^{13}\text{C}_{12}$ -PCB-141) for evaluation of recovery. Lipids were determined by evaporation of a fraction of each extract to a constant weight. The remainder of each extract was purified by gel permeation chromatography, with a $50\text{ cm} \times 2.5\text{ cm}$ i.d. glass column packed with 40 g SX-3 "Bio-Beads" (Bio-Rad Laboratories, Hercules, CA) and eluted with DCM/hexane (1/1 in volume) for lipid removal. The fraction eluting from 90 to 280 mL, containing PBDEs and other organohalogen compounds, was collected and concentrated. This fraction was further purified on 2-g silica gel solid-phase extraction columns (Isolute, International Sorbent Technology, UK). The first fraction eluted from the silica column with 3.5 mL of hexane was discarded. The second fraction, which contained PBDEs and other halogenated compounds, was obtained by elution with 6.5 mL of 60:40 hexane/DCM. Following solvent exchange to hexane, the second fraction was concentrated and spiked with internal standards ($^{13}\text{C}_{12}$ -PCB-208 and unlabeled PCB-82).

Samples were analyzed on a Shimadzu model 2010 gas chromatograph, coupled with a model QP2010 mass spectrometer (Shimadzu, Japan) using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A DB-XLB capillary column (J&W Scientific, Folsom, CA; $30\text{ m} \times 0.25\text{ mm}$ i.d., $0.25\text{ }\mu\text{m}$ film) was used to separate the PBDE congeners examined (1, 2, 3, 10, 7, 11, 8, 12, 13, 15, 30, 32, 17, 25, 33, 28, 35, 37, 75, 49, 47, 66, 77, 100, 119, 99, 116, 118, 155, 85, 126, 154, 153, 138, 166, 183, 181, 190). Methane was used as a chemical ionization moderating gas at an ion source pressure of 2.4×10^{-3} Pa. Carrier gas was helium, and $1\text{ }\mu\text{L}$ injections were made in the splitless mode. Initial column temperature was held at $110\text{ }^{\circ}\text{C}$ for 1 min, and then programmed to $180\text{ }^{\circ}\text{C}$ at $8\text{ }^{\circ}\text{C}/\text{min}$ (held for 1 min), to $240\text{ }^{\circ}\text{C}$ at $2\text{ }^{\circ}\text{C}/\text{min}$ (held for 5 min), to $280\text{ }^{\circ}\text{C}$ at $2\text{ }^{\circ}\text{C}/\text{min}$ (held for 25 min), and to $290\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$ (held for 13 min). A CP-Sil 13 CB ($12.5\text{ m} \times 0.25\text{ mm}$ i.d., $0.25\text{ }\mu\text{m}$ film) capillary column was used to separate BDE-197, -203, -196, -208, -207, -206, and -209. The oven temperature was programmed from 110 to $300\text{ }^{\circ}\text{C}$ at a rate of $8\text{ }^{\circ}\text{C}/\text{min}$ (held for 20 min). Ion fragments m/z 79 and 81 ($[\text{Br}]^{-}$) were monitored for all congeners except for BDE-209 for which m/z 79, 81, 486.7, and 488.7 were recorded. Fragments m/z 372, 374, and 376 were monitored for surrogate $^{13}\text{C}_{12}$ -PCB-141, and 474, 476,

and 478 were monitored for the internal standard $^{13}\text{C}_{12}$ -PCB-208. Quantification was performed using calibration curves made from standard solutions at 5–9 concentration levels. The limit of detection (LOD), defined as a signal of 5 times the noise level ($S/N = 3$ for BDE-209), ranged from 0.06 to 52.6 ng/g lipid weight for mono- to nona- congeners and from 1.20 to 105 for BDE-209, depending on the sample size.

QA/QC. Proper handling was employed from sample collection to chemical analysis to minimize the potential sample contamination, cross contamination, and PBDE degradation. Instrumental QC included regular injection of solvent blanks and standard solutions. The method QC was ensured through analysis of procedural blanks, blind triplicate samples, triplicate spiked blanks (PBDE standards spiked into sodium sulfate), and triplicate spiked matrices (PBDE standards spiked into pre-extracted samples). In total, 17 procedural blanks were analyzed sequentially with the samples. Only trace levels of BDE-47, -66, and -99 were detected in blanks and the mean values were subtracted from samples. BDE-209 was only detected in two blanks, but at nonquantifiable ($S/N < 3$) levels. Surrogate standard recoveries of $^{13}\text{C}_{12}$ -PCB-141 ranged from 80.7% to 110% ($\text{RSD} < 8\%$), after omission of a single outlier (59.7%). The percent relative standard deviations (%RSDs) for detected congeners were all $\leq 6\%$ in blind triplicate samples except for BDE-209 which had a RSD of 8.9%. The mean recoveries of ten individual congeners (28, 47, 66, 100, 99, 85, 154, 153, 138, and 183) spiked into pre-extracted matrices ranged from 70.2 to 108% ($\text{RSDs} < 8\%$). The mean recovery of BDE-209 was $82.0 \pm 7.9\%$ ($\text{RSD} < 10\%$) in triplicate spiked blanks.

Statistical Analysis. Among all screened PBDE congeners, only those with at least 65% of all measurements above the pertinent LOD were used in statistical analyses (i.e., BDE-28, -49, -47, -100, -119, -99, -118, -154, -153, -138, -183, -181, -203, -196, -208, -207, and -209). "ΣPBDEs" is defined here as the sum of these 17 congeners. For results less than the LOD, a value of one-half of the LOD was assigned. All levels were recovery corrected and are presented on a lipid weight (lw) basis. Levels or congener contributions are expressed as mean \pm standard error in the discussion. All concentration data were logarithmically transformed to approximate a normal distribution before inter-species statistical evaluations with ANOVA and Scheffe's post-hoc test (SPSS 13.0, SPSS Inc.). Data were further evaluated with principal components analysis (PCA), programmed with R Language (www.r-project.org). The level of significance was set at $\alpha = 0.05$ throughout this study. For each species, no significant relationship was observed between PBDE levels and any of the biological variables (i.e., body mass, age, sex). Thus, these variables were not used to correct or further subclassify data.

Results and Discussion

Concentration Data and Interspecies Comparisons. Among the species examined, ΣPBDE levels were highest in common kestrel (muscle $12\,300 \pm 5540$; liver $12\,200 \pm 6500$; pooled kidneys 5340 ng/g lw) (Figure 1). To date few reports have evaluated PBDE levels in avian kidneys. Maxima were detected in muscle ($31\,700\text{ ng/g lw}$) and liver ($40\,900\text{ ng/g lw}$) of a kestrel. These concentrations rival the highest reported in wildlife to date (6, 8). Large differences in PBDE levels among individual kestrels (ranging 279–31 700 in muscle and 126–40 900 ng/g lw in liver) suggest varying exposure. Previous avian studies on other organohalogen compounds have indicated that factors such as the individual's dietary habits, body condition, age, and sex may be important (23). The sparrowhawks (*Accipiter nisus*) contained ΣPBDEs of 5690 ± 1890 in muscle and $5550 \pm 2220\text{ ng/g lw}$ in liver. Their pooled kidneys had ΣPBDEs of 4020 ng/g lw . While these levels were statistically similar to the Chinese

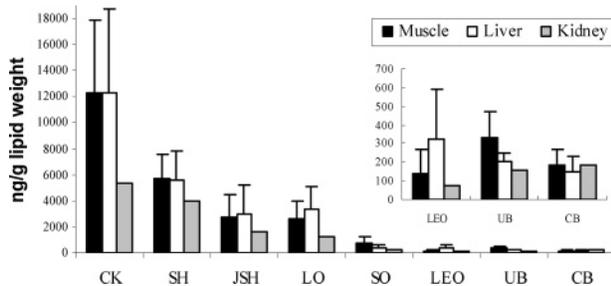


FIGURE 1. Mean Σ PBDE levels (ng/g lipid weight) in various tissues of eight bird species from Northern China. Error bars represent one standard error, except for kidney where samples were pooled by species. Species abbreviations: CK = common kestrel ($N = 6$); SH = sparrowhawk ($N = 11$); JSH = Japanese sparrowhawk ($N = 6$); LO = little owl ($N = 6$); SO = scops owl ($N = 6$); LEO = long-eared owl ($N = 6$); UB = upland buzzard ($N = 3$); CB = common buzzard ($N = 3$).

kestrel burdens, another study reported significantly higher levels in Belgian sparrowhawks than kestrels (24). The authors of that study suggested that the interspecies contaminant differences might be due to varying dietary habits. Sparrowhawks feed primarily on small birds. Kestrel diet consists mainly of insects and small animals, normally with a modest contribution from small birds (25). Additional factors (e.g., migratory habits) may have contributed to the different results in the two studies. Kestrels examined in the present study are believed to remain mainly in the Beijing area year round, establishing nests and foraging in urban fringes or urban centers. Sparrowhawks are migrants and tend to spend several months per year in rural areas well north of China, such as Siberia. Therefore kestrels may have greater exposure to Chinese urban PBDE sources. Perhaps due to their migratory behavior, sparrowhawks in the present study contained statistically higher Σ DDT levels relative to kestrels (unpublished data). A similar species, the Japanese sparrowhawk (*Accipiter gularis*), contained mean Σ PBDEs of 2740 ± 1740 in muscle and 2990 ± 2220 ng/g lw in liver. These levels were statistically similar to those in *Accipiter nisus*, perhaps related to comparable dietary and migratory habits. Buzzards and some of the Chinese owls examined contained statistically lower PBDE burdens than sparrowhawks. Upland buzzards exhibited 329 ± 137 of Σ PBDEs in muscle and 205 ± 42.4 ng/g lw in liver. Common buzzards contained PBDEs within the same magnitude (182 ± 87.3 in muscle and 151 ± 78.4 ng/g lw in liver), as did long-eared owls (141 ± 122 in muscle and 319 ± 273 ng/g lw in liver). Scops owls had slightly elevated levels (muscle 793 ± 481 ; liver 428 ± 192 ng/g lw). Owls and buzzards have similar dietary habits, feeding mainly on small mammals such as mice, field voles, rats, and insects (25, 26). Avian prey constitute a small percentage of their diet and this might contribute to the 1–2 orders of magnitude lower body burdens versus those in sparrowhawks. Among the three owl species, little owls (*Athene noctua*) contained significantly higher Σ PBDEs in muscle (2630 ± 1300 ng/g lw) and liver (3350 ± 1800 ng/g lw) than scops and long-eared owls. Little owls are year-round residents in the Beijing area, whereas the other two species migrate (26). Hence longer exposure to Chinese urban PBDE sources might contribute to the higher levels in little owls. A previous study has reported a decrease in air PBDE concentrations along a Canadian urban–rural transect (27). Though they are both residents in Beijing, little owls contained lower levels than common kestrels. Little owls prefer to build their nests in forests located in parks or suburban areas. Kestrels are more active in the urban center areas, building their nests on man-made structures. More intimate contact with human activities may increase the kestrels' exposure to urban PBDE sources. Different biotransformation or uptake

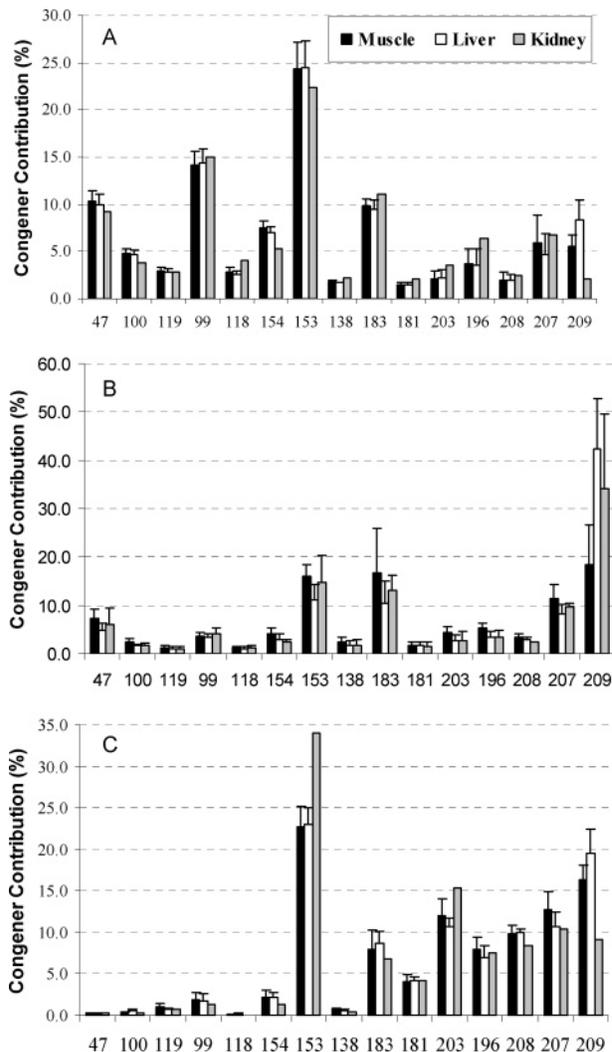


FIGURE 2. Congener profiles in various tissues of sparrowhawk (A), buzzard (B), and common kestrel (C). BDE-28 and -49 were excluded from these profiles due to their modest contributions (ranging from 0.01% to 1.44%). Profiles for other species are listed in the Supporting Information.

capacities may also contribute to the inter-species differences. Small sample size and individual exposure history, as well as varying age, sex, or body condition, may further confound comparisons. Inclusion of different PBDE congeners in the totals presented in other published bird studies may also contribute. The Chinese kestrels had mean muscle and liver PBDE levels much higher than those reported for avian species from other countries (i.e., 10–1000x those in Belgian birds and in peregrine falcon eggs from Greenland (22, 24, 28), 10–100x those in cormorants and herons from UK and in Norwegian eggs from various species (29–31), 10x those in Swedish peregrine falcon and guillemot eggs and in Japanese cormorant eggs (20, 32, 33), and 1–10x those in eggs of various aquatic species from North America (34–36)). However, some of the studies referenced had maxima in individual birds of the same magnitude as those reported in our study.

Congener Profiles and PCA. Distinct congener profiles were observed among the different species examined (Figure 2 and Figure SI-1). Profiles were generally dominated by the more brominated congeners. This differs dramatically from what has been observed in fish and piscivorous birds where BDE-47 usually dominates (8). Profiles in muscle and liver of Chinese sparrowhawks were dominated by BDE-153, followed by -99, with lesser contributions from -47, -183,

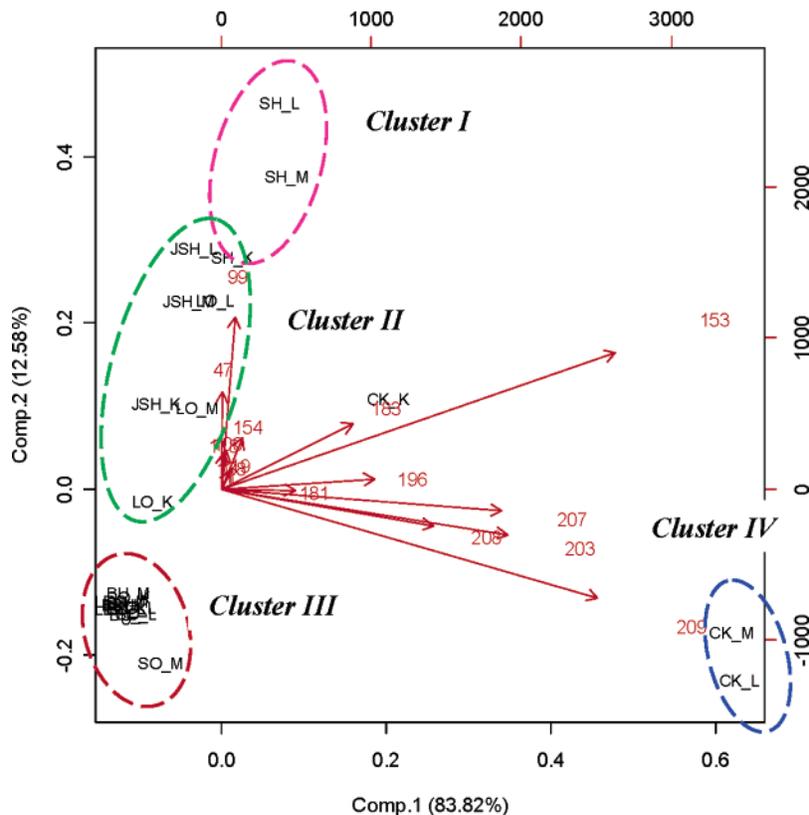


FIGURE 3. Biplot from the Principle Component Analysis (Comp. 1, 83.82% variance; Comp. 2, 12.58% variance). Species identification: CK = common kestrel; SH = sparrowhawk; JSH = Japanese sparrowhawk; LO = little owl; SO = scops owl; LEO = long-eared owl; BU = buzzard (upland and common buzzard). Tissue identification: _M = muscle; _L = liver; _K = kidney.

and -154, -209, and -207. Similar profiles were found in little owls. These distributions are similar to those reported in other raptor studies (20, 22) except that slightly elevated BDE-209 contributions were present in our samples. In muscle and liver of Japanese sparrowhawks collected in China, BDE-99, -153, and -47 were the major congeners (at roughly equivalent concentrations). These were followed by BDE-209, -207, and -183. Elevated contributions from BDE-99 and -153 were found in pooled kidneys relative to other tissues. Because the two buzzard species had statistically similar Σ PBDE levels and congener profiles and sample size was limited ($N = 3$ each), they are discussed together here. Buzzards exhibited roughly similar contributions of BDE-209, -183, and -153 in muscle. These congeners were dominant in this tissue, followed by -207 and -47. In liver and kidney, BDE-209 was the major congener, followed by -153, -183, -207, and -47. Long-eared owls had profiles similar to those of buzzards as follows: -153 > -209 > -183 \approx -47 \approx -99 > -207 \approx -208 in muscle; -209 > -153 \approx -207 > -208 > -183 > -47 \approx -99 in liver; -209 > -153 > -99 \approx -47 > -183 > -154 \approx -118 in kidney. Contributions by congeners with six or more bromines ranged from 71.8% to 98.6% in buzzards and 58.3% to 91.5% in long-eared owls. Voorspoels et al. reported that in Belgian owls and buzzards BDE-47, -99, and -153 were the most abundant congeners, each contributing between 15% and 35% to the Σ PBDEs (22). Our findings may indicate a greater prevalence of deca- through octa-BDEs in China. Congeners in Chinese scops owls prevailed in the following order: muscle -209 > -153 > -99 > -47 \approx -207 > -208 \approx -183; liver -209 > -207 \approx -153 \approx -208 > -99 > -183 > -47; kidney -209 > -153 > -99 > -183 > -47 > -208 \approx -207. BDE-153 was the dominant congener in the three tissues examined in the kestrels, followed by -209 > -207 \geq -203 \geq -208 > -183 \geq -196 in muscle and liver; and by -203 > -207 > -209 > -208 > -196 > -183 in kidney. The sum of the

individual contributions of BDE-207, -208, -203, and -196 in kestrels was as much as 57.6% of Σ PBDEs, whereas the BDE-47 percentages were as low as 0.01%. Biotransformation in kestrels may be responsible for the modest BDE-47 percentages. This view is supported by a recent lab study wherein kestrel nestlings were fed a penta- mixture (predominantly BDE-47) daily (37). After 36 days, kestrels contained greater amounts of BDE-100 and -99 than BDE-47 (37). In contrast to the Chinese kestrels, elevated BDE-47 contributions were reported in Belgian kestrels, representing approximately 9% of liver and 5% of muscle PBDE burdens (24). However, this comparison may be confounded by the fact that different numbers of congeners were summed in these studies (17 vs 8), as well as the small sample sizes available ($N = 6$ and 3, respectively).

PCA provides an informative visual display, facilitating inter-species comparisons. The biplot of PCA displays four clusters (Figure 3). Clusters I (sparrowhawk) and II (Japanese sparrowhawk and little owl) appeared enriched in BDE-99, -47, and other less brominated congeners relative to the other clusters. Preferential excretion or metabolism of higher brominated congeners may be suggested for these species. Alternatively, it may be a function of exposure. Cluster IV (kestrel) tended to be enriched in BDE-209 and some nona- and octa- congeners, relative to the other clusters. The score point of kestrel kidney was located outside of the kestrel cluster (muscle and liver samples), indicating a significant difference in congener levels and profiles between these tissues. Species included in Cluster III (buzzard, scops owl, and long-eared owl) were similar in terms of levels and profiles, as reflected by their overlapping positions in the biplot. Clusters I, III, and IV separated well from each other, indicative of significantly different profiles.

BDE-209. Deca- has historically been the dominant PBDE product in terms of market demand and remains widely used

worldwide. While production and usage of the penta- and octa- mixtures have been discontinued in several countries, the European Commission exempted deca- in 2005 from inclusion in the Restrictions on Hazardous Substances Used in Electrical and Electronics Applications Directive. Examination of available published data indicated modest toxicity in most studies and limited bioaccumulation potential. BDE-209 has been less frequently reported in wildlife than constituents of penta-. However, some studies have indicated that BDE-209 can be degraded, principally photochemically or via biotransformation mechanisms, to less brominated congeners that are more bioavailable and toxic (8). Interestingly, BDE-209 has been detected with greater frequency in terrestrial versus aquatic wildlife, albeit generally at low concentrations. In terrestrial mammals such as grizzly bears and red foxes, BDE-209 has been the dominant congener in some specimens, with levels up to 41.7 and 760 ng/g lw, respectively (38, 39). BDE-209 has been reported more frequently in avian species. For example, it was detectable in 6 out of 44 livers from Belgian buzzards, sparrowhawks, and owls (up to 190 ng/g lw) and 19 out of 25 serum samples (up to 58 ng/g lw) (22). de Boer et al. reported BDE-209 levels up to 412 ng/g lw in eggs of kestrels, sparrowhawks, and peregrine falcons from the UK and Sweden (21). Other falcon egg studies found BDE-209 levels ranging from 3.8 to 250 ng/g lw in a South Greenland population and <20 to 430 in Swedish birds (20, 28).

Compared to previous reports, the Chinese raptors contained remarkably higher burdens of the more brominated congeners, including BDE-209. BDE-209 could be quantified in 79.4% of all tissues examined. Especially high levels were found in muscle (2150 ± 1040 ng/g lw) and liver (2870 ± 1930 ng/g lw) of common kestrels. One specimen contained 6220 ng/g lw in muscle and 12 200 in liver, which are among the highest BDE-209 levels reported in wildlife to date. It has been reported that BDE-209 levels in urban air samples from China were higher than those in North American and European studies (15). The pooled kidneys of kestrels had a lower percentage of BDE-209 (as well as elevated contributions from -153) relative to other tissues. Similar results were also found in Japanese sparrowhawks. Buzzards and long-eared owls generally contained the lowest levels (11–133 and <1.2–528 ng/g lw, respectively) among the raptors examined here. Nonetheless, in specimens of these species where BDE-209 was detectable it was a dominant congener. BDE-209 was detected in all buzzards with contributions up to 71.0% of the Σ PBDEs. It was also dominant in 3 of 6 liver tissues of long-eared owls with contributions up to 72.0%, and in 3 of 6 muscle tissues of scops owls with contributions as high as 84.0%. These results reinforce the growing view that significant bioaccumulation of BDE-209 can occur in some terrestrial food chains, especially when abundant deca- sources are present. Interestingly, species with the highest PBDE burdens generally had lower BDE-209 relative contributions (i.e., < 29.9% in kestrels and <26.9% in sparrowhawks) than less contaminated birds (i.e., buzzards and some owls) (Figure 4). Statistically, higher relative BDE-209 contributions in liver were found in buzzards ($p = 0.039$) and long-eared owls ($p = 0.043$) relative to sparrowhawks, respectively. Among the three owl species, little owls had much higher Σ PBDEs but statistically lower BDE-209 contributions. This pattern may relate to differences in uptake or metabolism of individual PBDE congeners between the different species.

Potential PBDE Sources. The levels and congener profiles observed in the present study may relate to the significant production, usage, and disposal of deca-containing products in China. While little penta- has reputedly been used in Asia (150 metric tons (MT) in 2001) relative to the past major consumer, North America (7100 MT), similar demands for

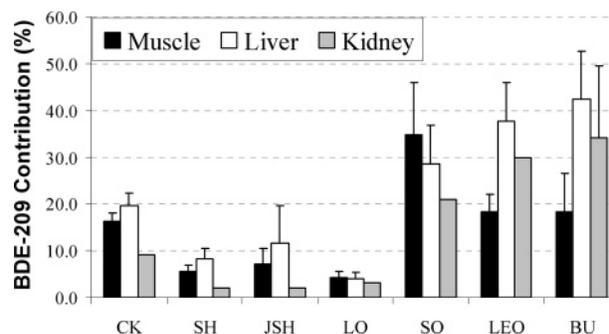


FIGURE 4. Relative contributions of BDE-209 to Σ PBDEs in various raptors. Species identification: CK = common kestrel; SH = sparrowhawk; JSH = Japanese sparrowhawk; LO = little owl; SO = scops owl; LEO = long-eared owl; BU = buzzard (upland and common buzzard).

deca- were reported (23 000 and 24 500 MT, respectively) (10). Data from the 2001 U.S. EPA's Toxics Reduction Inventory (TRI) on estimated industrial emissions in the United States suggested that the textile industry released the most deca- to the surface water, air, and publicly owned wastewater treatment works (POTWs), followed by the chemical industry, electronics, and plastics industries (5). No comparable data are available for China. However, all these industries are substantial in China. Considerable production is eventually exported to North American and European markets where fire retardancy regulations have been historically strict.

The raptors sampled in the current study were mostly from relatively urbanized areas. Due to expanding human development and the mobility of these birds, the likelihood of their encountering contaminants is high and increasing. For example, some raptors roost on man-made structures (e.g., chimneys or towers) and incorporate synthetic materials such as plastics in their nests. Hence the potential of exposure from urban-related PBDE sources is accentuated. Uptake may be direct via exposure to products or degradates or via the food chain by consuming prey that come in contact with these materials. To illustrate, crickets have been observed to consume penta-laden polyurethane furniture foam and pass PBDEs to frogs that in turn preyed upon them (40). Similar exposure scenarios likely occur for other insects, small mammals, and birds that constitute the raptor diet. Clearly, a better understanding of the potential sources of PBDEs to the Chinese environment in general and to birds of prey in particular is required.

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Supporting Information Available

Descriptive information on the birds and more detailed congener data (mean and standard deviation) by species in Tables SI-1 and SI-2, respectively. Congener profiles for Japanese sparrowhawk and three owl species are provided in Figure SI-1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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